Data collection

Nicolet *R*3 diffractometer
ω scans
Absorption correction: none
2707 measured reflections
2587 independent reflections
2342 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0089$

$\theta_{\rm max} = 25°$
$h = -10 \rightarrow 0$
$k = -10 \rightarrow 11$
$l = -12 \rightarrow 12$
3 standard reflections
every 147 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0301$
$wR(F^2) = 0.0811$
$S = 1.038$
2587 reflections
181 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.4395P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.381$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.340$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S1—C2	1.811 (3)	P3—C7	1.792 (2)
S1—C6	1.812 (2)	O4—P5	1.619 (2)
C2—P3	1.808 (2)	P5—O3	1.472 (2)
P3—O2	1.471 (2)	P5—C13	1.786 (2)
P3—O4	1.6060 (14)	P5—C6	1.795 (2)
C2—S1—C6	98.78 (9)	P3—O4—P5	137.12 (9)
P3—C2—S1	114.71 (11)	O3—P5—O4	113.26 (9)
O2—P3—O4	110.78 (9)	O3—P5—C13	113.54 (9)
O2—P3—C7	112.18 (9)	O4—P5—C13	102.83 (9)
O4—P3—C7	105.28 (8)	O3—P5—C6	113.94 (9)
O2—P3—C2	112.58 (10)	O4—P5—C6	102.51 (9)
O4—P3—C2	105.26 (9)	C13—P5—C6	109.68 (9)
C7—P3—C2	110.28 (9)	P5—C6—S1	109.17 (10)
C6—S1—C2—P3	63.50 (12)	P3—O4—P5—C6	−37.50 (14)
S1—C2—P3—O4	−39.13 (12)	O4—P5—C6—S1	58.06 (11)
C2—P3—O4—P5	27.71 (14)	C2—S1—C6—P5	−73.53 (11)

Data collection: *P*3 *Software* (Nicolet, 1987). Cell refinement: *P*3 *Software*. Data reduction: *XDISK* in *P*3 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

The crystals of (I) were kindly provided by Professor M. Fild and Dr M. Sebastian of this Institute. We thank the Fonds der Chemischen Industrie for financial support.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1232). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 616–620

3-Acetonylbicyclo[6.3.0]undecane-2,6-dione, (I), 7-Acetonyl-4,4-dimethylbicyclo[6.3.0]undecane-2,6-dione, (II), 7,12-Dihydroxy-12-methyltetracyclo[8.2.1.0^{1,5}.0^{7,11}]tridecan-13-one Monohydrate, (III), and 8,8-Dimethyltricyclo[9.3.0.0^{2,6}]tetradec-5-ene-4,10-dione, (IV)

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Abstract

The crystal structures of the four title compounds, $C_{14}H_{20}O_3$, (I), $C_{16}H_{24}O_3$, (II), $C_{14}H_{20}O_3.H_2O$, (III), and $C_{16}H_{22}O_2$, (IV), which were obtained during studies of the preparation of C_5–C_8–C_5 fused-ring compounds, have been determined by X-ray diffraction.

Comment

The synthesis of C_5–C_8–C_5 fused-ring compounds by intramolecular aldol reaction has been investigated (Umehara *et al.*, 1993; Kawata *et al.*, 1993). Although a C_5–C_6–C_5–C_5 tetracyclic compound, (III), was obtained from (I), the desired C_5–C_8–C_5 fused-ring compound (IV) was yielded from (II). Epimerization of (II) seems to occur under basic conditions. A strain-energy calculation by *MM*2 (Allinger, 1977) indicates that structure (IV) is more stable than the epimer by 21.8 kJ mol^{-1}. The eight-membered ring adopts a boat–chair form in compounds (I) and (IV), and a chair–chair form in compound (II). The crystal of (III) was obtained as the monohydrate and there are intermolecular O—H···O hydrogen bonds (see Table 4). The six-membered ring of compound (III) has a flattened boat form and the O17

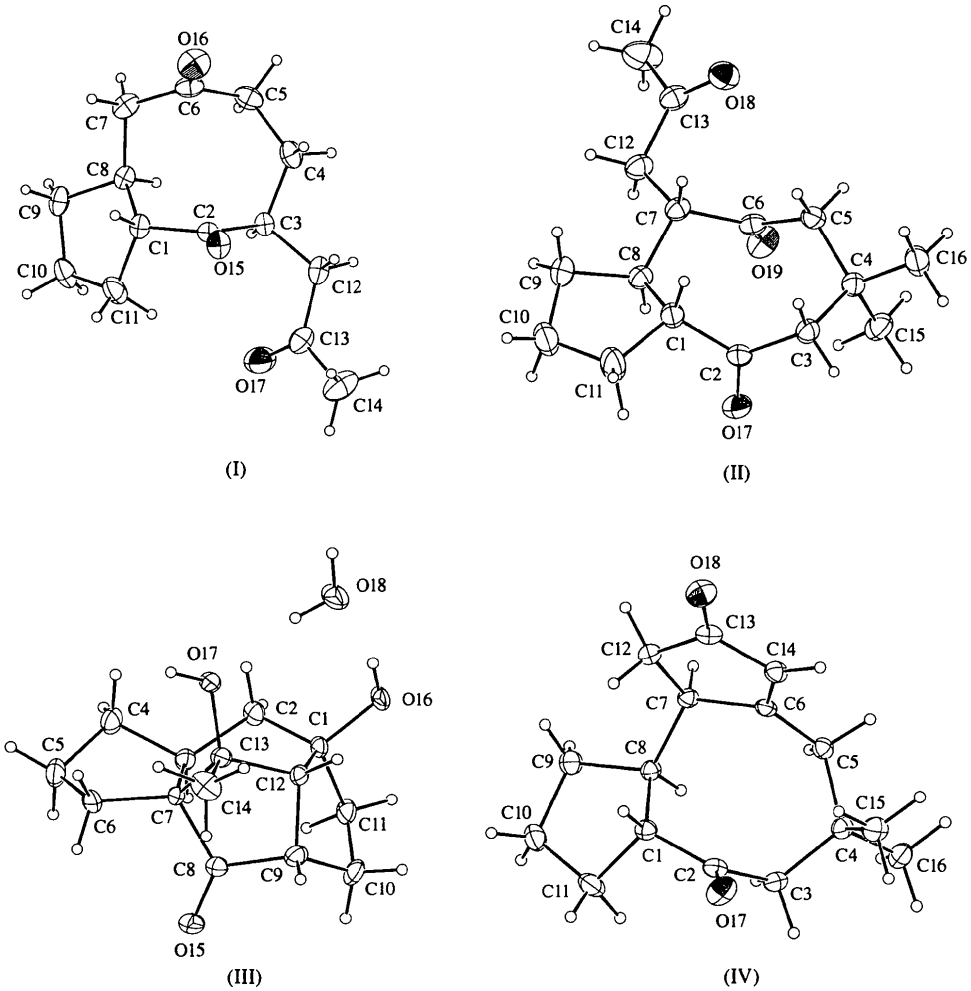
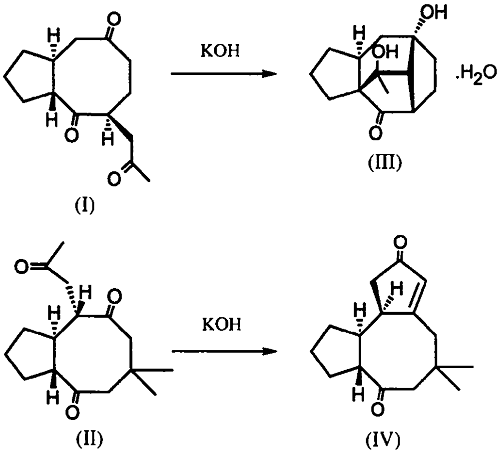


Fig. 1. The molecular structures of compounds (I)–(IV), with displacement ellipsoids at the 20% probability level. H atoms are represented by circles of radius 0.1 Å.

atom is fairly close to one of the H atoms bonded to C2 [O17···H2*B* 2.29 (2) Å].



Experimental

The melting points of the title compounds are (I) 370, (II) 380, (III) 396 and (IV) 461 K.

Compound (I)

Crystal data

$C_{14}H_{20}O_3$
$M_r = 236.31$
Monoclinic
$P2_1/a$
$a = 10.267\,(1)$ Å
$b = 8.505\,(1)$ Å
$c = 14.996\,(1)$ Å
$\beta = 96.85\,(1)°$
$V = 1300.1\,(2)$ Å^3
$Z = 4$
$D_x = 1.207$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–$15°$
$\mu = 0.083$ mm^{-1}
$T = 298$ K
Prism
0.50 × 0.50 × 0.40 mm
Colourless

Data collection

Rigaku AFC-5 diffractometer
θ–2θ scans
Absorption correction: none
3157 measured reflections
2985 independent reflections
1834 reflections with $|F_o| > 3\sigma(|F_o|)$

$R_{\rm int} = 0.011$
$\theta_{\rm max} = 26.4°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 11$
$l = -19 \rightarrow 19$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.0605$
$wR = 0.0529$
$S = 1.16$
1834 reflections
234 parameters
All H atoms refined
$w = 1/[\sigma^2(F) + 0.000225F^2]$

$(\Delta/\sigma)_{\rm max} = 0.059$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °) for (I)*

C1—C2	1.501 (3)	C6—C7	1.493 (3)
C1—C8	1.538 (3)	C6—O16	1.220 (2)
C1—C11	1.542 (3)	C7—C8	1.522 (3)
C2—C3	1.514 (2)	C8—C9	1.519 (3)
C2—O15	1.223 (2)	C9—C10	1.521 (4)
C3—C4	1.543 (3)	C10—C11	1.540 (4)
C3—C12	1.537 (3)	C12—C13	1.493 (3)
C4—C5	1.536 (3)	C13—C14	1.502 (4)
C5—C6	1.494 (3)	C13—O17	1.189 (3)
C2—C1—C8	118.4 (2)	C7—C6—O16	121.5 (2)
C2—C1—C11	110.8 (2)	C6—C7—C8	112.2 (2)
C8—C1—C11	103.9 (2)	C1—C8—C7	114.4 (2)
C1—C2—C3	121.3 (2)	C1—C8—C9	102.4 (2)
C1—C2—O15	119.4 (2)	C7—C8—C9	114.4 (2)
C3—C2—O15	119.3 (2)	C8—C9—C10	104.0 (2)
C2—C3—C4	110.6 (2)	C9—C10—C11	105.9 (2)
C2—C3—C12	110.2 (2)	C1—C11—C10	106.0 (2)
C4—C3—C12	108.1 (2)	C3—C12—C13	115.0 (2)
C3—C4—C5	118.1 (2)	C12—C13—C14	116.1 (3)
C4—C5—C6	113.6 (2)	C12—C13—O17	122.5 (2)
C5—C6—C7	117.9 (2)	C14—C13—O17	121.3 (3)
C5—C6—O16	120.6 (2)		

Compound (II)

Crystal data

$C_{16}H_{24}O_3$
$M_r = 264.37$
Triclinic
$P\overline{1}$
$a = 9.966$ (2) Å
$b = 10.794$ (2) Å
$c = 8.171$ (2) Å
$\alpha = 98.03$ (2)°
$\beta = 111.46$ (2)°
$\gamma = 106.98$ (2)°
$V = 751.8$ (3) Å^3
$Z = 2$
$D_x = 1.168$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 14.5$–$14.9°$
$\mu = 0.079$ mm^{-1}
$T = 297$ K
Prism
0.60 × 0.50 × 0.40 mm
Colourless

Data collection

Rigaku AFC-5 diffractometer
θ–2θ scans
Absorption correction: none
3640 measured reflections
3443 independent reflections
2454 reflections with $|F_o| > 3\sigma(|F_o|)$

$R_{\rm int} = 0.010$
$\theta_{\rm max} = 27.5°$
$h = 0 \rightarrow 12$
$k = -14 \rightarrow 13$
$l = -10 \rightarrow 9$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.0537$
$wR = 0.0470$
$S = 1.00$
2454 reflections
259 parameters
All H atoms refined
$w = 1/[\sigma^2(F) + 0.000225F^2]$

$(\Delta/\sigma)_{\rm max} = 0.069$
$\Delta\rho_{\rm max} = 0.17$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 2. *Selected geometric parameters (Å, °) for (II)*

C1—C2	1.515 (1)	C6—C7	1.529 (1)
C1—C8	1.539 (1)	C6—O19	1.214 (1)
C1—C11	1.537 (2)	C7—C8	1.532 (2)
C2—C3	1.498 (2)	C7—C12	1.520 (1)
C2—O17	1.213 (1)	C8—C9	1.531 (2)
C3—C4	1.546 (2)	C9—C10	1.512 (2)
C4—C5	1.548 (1)	C10—C11	1.494 (2)
C4—C15	1.527 (2)	C12—C13	1.494 (2)
C4—C16	1.530 (2)	C13—C14	1.503 (2)
C5—C6	1.507 (1)	C13—O18	1.208 (1)
C2—C1—C8	113.2 (1)	C5—C6—O19	121.1 (1)
C2—C1—C11	112.6 (1)	C7—C6—O19	119.1 (1)
C8—C1—C11	104.9 (1)	C6—C7—C8	109.1 (1)
C1—C2—C3	119.3 (1)	C6—C7—C12	109.9 (1)
C1—C2—O17	119.5 (1)	C8—C7—C12	112.9 (1)
C3—C2—O17	121.2 (1)	C1—C8—C7	113.9 (1)
C2—C3—C4	114.8 (1)	C1—C8—C9	102.9 (1)
C3—C4—C5	110.9 (1)	C7—C8—C9	115.8 (1)
C3—C4—C15	110.4 (1)	C8—C9—C10	104.8 (1)
C3—C4—C16	107.0 (1)	C9—C10—C11	107.2 (1)
C5—C4—C15	112.2 (1)	C1—C11—C10	107.1 (1)
C5—C4—C16	107.0 (1)	C7—C12—C13	113.6 (1)
C15—C4—C16	109.1 (1)	C12—C13—C14	117.0 (1)
C4—C5—C6	118.5 (1)	C12—C13—O18	121.9 (1)
C5—C6—C7	119.8 (1)	C14—C13—O18	121.1 (1)

Compound (III)

Crystal data

$C_{14}H_{20}O_3.H_2O$
$M_r = 254.33$
Monoclinic
$P2_1/n$
$a = 8.115$ (2) Å
$b = 17.959$ (2) Å
$c = 9.034$ (2) Å
$\beta = 94.71$ (2)°
$V = 1312.1$ (4) Å^3
$Z = 4$
$D_x = 1.287$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–$15°$
$\mu = 0.093$ mm^{-1}
$T = 298$ K
Prism
0.50 × 0.50 × 0.40 mm
Colourless

Data collection

Rigaku AFC-5 diffractometer

$R_{\rm int} = 0.019$
$\theta_{\rm max} = 25.0°$

θ–2θ scans
Absorption correction: none
2477 measured reflections
2309 independent reflections
1593 reflections with $|F_o| > 3\sigma(|F_o|)$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 21$
$l = -10 \rightarrow 10$
3 standard reflections every 100 reflections intensity decay: 3.2%

Refinement

Refinement on F
$R = 0.0564$
$wR = 0.0538$
$S = 1.24$
1593 reflections
251 parameters
All H atoms refined
$w = 1/[\sigma^2(F) + 0.000225F^2]$
$(\Delta/\sigma)_{\max} = 0.059$
$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 3. *Selected geometric parameters (Å, °) for (III)*

C1—C2	1.522 (4)	C7—C8	1.519 (3)
C1—C11	1.543 (4)	C7—C13	1.539 (3)
C1—C12	1.564 (3)	C8—C9	1.527 (3)
C1—O16	1.437 (3)	C8—O15	1.213 (3)
C2—C3	1.526 (4)	C9—C10	1.532 (4)
C3—C4	1.538 (4)	C9—C12	1.536 (3)
C3—C7	1.567 (3)	C10—C11	1.499 (4)
C4—C5	1.524 (5)	C12—C13	1.541 (3)
C5—C6	1.510 (4)	C13—C14	1.524 (4)
C6—C7	1.545 (4)	C13—O17	1.433 (3)
C2—C1—C11	109.7 (2)	C8—C7—C13	100.4 (2)
C2—C1—C12	112.0 (2)	C7—C8—C9	109.6 (2)
C2—C1—O16	110.8 (2)	C7—C8—O15	126.0 (2)
C11—C1—C12	106.3 (2)	C9—C8—O15	124.4 (2)
C11—C1—O16	106.5 (2)	C8—C9—C10	114.8 (3)
C12—C1—O16	111.2 (2)	C8—C9—C12	101.9 (2)
C1—C2—C3	111.4 (2)	C10—C9—C12	104.9 (3)
C2—C3—C4	115.4 (2)	C9—C10—C11	103.6 (3)
C2—C3—C7	114.6 (2)	C1—C11—C10	107.0 (3)
C4—C3—C7	103.4 (2)	C1—C12—C9	103.3 (2)
C3—C4—C5	103.2 (2)	C1—C12—C13	115.3 (2)
C4—C5—C6	103.9 (3)	C9—C12—C13	102.6 (2)
C5—C6—C7	107.4 (3)	C7—C13—C12	99.9 (2)
C3—C7—C6	104.9 (2)	C7—C13—C14	112.2 (2)
C3—C7—C8	107.6 (2)	C7—C13—O17	113.7 (2)
C3—C7—C13	110.8 (2)	C12—C13—C14	112.0 (2)
C6—C7—C8	115.4 (2)	C12—C13—O17	110.2 (2)
C6—C7—C13	117.6 (2)	C14—C13—O17	108.8 (2)

Table 4. *Hydrogen-bonding geometry (Å, °) for (III)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O16—H16···O18	0.83 (3)	1.95 (3)	2.763 (3)	164 (2)
O17—H17···O16^{i}	0.77 (3)	2.03 (2)	2.791 (3)	169 (2)
O18—H18*A*···O15^{ii}	0.84 (3)	2.04 (2)	2.867 (3)	170 (3)
O18—H18*B*···O17	0.84 (3)	1.97 (3)	2.780 (3)	164 (3)

Symmetry codes: (i) $x - \frac{1}{2}, \frac{3}{2} - y, \frac{1}{2} + z$; (ii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

Compound (IV)

Crystal data

$C_{16}H_{22}O_2$
$M_r = 246.35$
Triclinic
$P\overline{1}$
$a = 8.689$ (2) Å
$b = 13.862$ (2) Å
$c = 5.960$ (1) Å
$\alpha = 94.12$ (1)°
$\beta = 100.47$ (1)°
$\gamma = 107.70$ (1)°
$V = 666.3$ (2) Å^3
$Z = 2$
$D_x = 1.228$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 13.5$–14.8°
$\mu = 0.079$ mm^{-1}
$T = 296$ K
Prism
0.7 × 0.2 × 0.15 mm
Colourless

Data collection

Rigaku AFC-5 diffractometer
θ–2θ scans
Absorption correction: analytical
$T_{\min} = 0.985$, $T_{\max} = 0.989$
2511 measured reflections
2345 independent reflections
1720 reflections with $|F_o| > 3\sigma(|F_o|)$
$R_{\rm int} = 0.012$
$\theta_{\max} = 25.0$°
$h = 0 \rightarrow 10$
$k = -16 \rightarrow 15$
$l = -7 \rightarrow 6$
3 standard reflections every 100 reflections intensity decay: 2.4%

Refinement

Refinement on F
$R = 0.0439$
$wR = 0.0406$
$S = 0.969$
1720 reflections
251 parameters
All H atoms refined
$w = 1/[\sigma^2(F) + 0.000225F^2]$
$(\Delta/\sigma)_{\max} = 0.02$
$\Delta\rho_{\max} = 0.14$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 5. *Selected geometric parameters (Å, °) for (IV)*

C1—C2	1.505 (2)	C6—C7	1.519 (2)
C1—C8	1.529 (2)	C6—C14	1.335 (2)
C1—C11	1.543 (2)	C7—C8	1.534 (2)
C2—C3	1.505 (2)	C7—C12	1.533 (2)
C2—O17	1.222 (2)	C8—C9	1.533 (2)
C3—C4	1.550 (2)	C9—C10	1.524 (2)
C4—C5	1.554 (2)	C10—C11	1.520 (2)
C4—C15	1.537 (2)	C12—C13	1.512 (2)
C4—C16	1.529 (2)	C13—C14	1.454 (2)
C5—C6	1.498 (2)	C13—O18	1.219 (2)
C2—C1—C8	118.3 (1)	C7—C6—C14	111.7 (1)
C2—C1—C11	110.6 (1)	C6—C7—C8	113.9 (1)
C8—C1—C11	101.7 (1)	C6—C7—C12	103.6 (1)
C1—C2—C3	120.5 (1)	C8—C7—C12	116.0 (1)
C1—C2—O17	119.6 (1)	C1—C8—C7	116.1 (1)
C3—C2—O17	119.8 (1)	C1—C8—C9	103.3 (1)
C2—C3—C4	115.3 (1)	C7—C8—C9	114.9 (1)
C3—C4—C5	113.0 (1)	C8—C9—C10	106.1 (1)
C3—C4—C15	110.2 (1)	C9—C10—C11	106.3 (2)
C3—C4—C16	107.4 (1)	C1—C11—C10	104.9 (1)
C5—C4—C15	110.6 (1)	C7—C12—C13	105.6 (1)
C5—C4—C16	107.1 (1)	C12—C13—C14	107.3 (1)
C15—C4—C16	108.4 (1)	C12—C13—O18	125.2 (1)
C4—C5—C6	118.6 (1)	C14—C13—O18	127.5 (1)
C5—C6—C7	121.3 (1)	C6—C14—C13	111.4 (1)
C5—C6—C14	126.9 (1)		

All H atoms were located on difference syntheses except for those bonded to the C14 atom in compound (II), whose positions were calculated geometrically and restrained to keep a C—H distance of 0.96 Å.

For all compounds, data collection: *AFC/MSC Diffractometer Control System* (Rigaku Corporation, 1993); cell refinement: *AFC/MSC Diffractometer Control System*; data reduction: local programs; program(s) used to solve structure: *CRYSTAN-GM* (Edwards, Gilmore, Mackay & Stewart, 1995); program(s) used to refine structure: *CRYSTAN-GM*; molecular graphics: *CRYSTAN-GM*; software used to prepare material for publication: *CRYSTAN-GM*.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: OA1017). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(*E*)-*o*-Stilbenecarboxylic Acid and its *p*-Methyl, Chloro and Methoxy Derivatives

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Abstract

The crystal structures of the title compounds, (*E*)-stilbene-1-carboxylic acid, $C_{15}H_{12}O_2$, (I*a*), (*E*)-4′-methylstilbene-1-carboxylic acid, $C_{16}H_{14}O_2$, (I*b*), (*E*)-4′-chlorostilbene-1-carboxylic acid, $C_{15}H_{11}ClO_2$, (I*c*) and (I*c*′), and (*E*)-4′-methoxystilbene-1-carboxylic acid, $C_{16}H_{14}O_3$, (I*d*), have been determined. The chloro derivative shows polymorphism, with prisms, (I*c*), being obtained from ether/hexane solution and needle crystals, (I*c*′), being obtained from ethanol solution. The latter is isostructural with (I*d*). The selectivities of the products to the addition reaction of bromine are different, however, suggesting that the bromonium ion intermediate is stabilized by a resonance contribution of the *p*-MeO group.

Comment

Reaction of (*E*)-*o*-stilbenecarboxylic acid, (I*a*), with bromine in solution gives *trans*-4-bromo-3-phenyl-3,4-dihydroisocoumarin, (IV*a*), as the major product through the intramolecular attack of a carboxylic acid O atom on the carbenium ion C atom of the bromonium ion intermediate (II*a*), along with *erythro*-1,2-dibromo-1,2-dihydro-*o*-stilbenecarboxylic acid, (III*a*) (Berti, 1958). When the bromination was carried out in AcOH, $CHCl_3$ and CH_2Cl_2, compound (IV*a*) was produced as the major product, although the reaction in CCl_4 at 263 K gave compound (III*a*) as the major product. Nevertheless, it is difficult to control the reaction in solution completely. On the other hand, the reaction can be controlled perfectly when carried out in the solid state. Treatment of powdered (I*a*) with bromine vapour or with powdered pyridine.HBr.Br_2 complex in the solid state at room temperature gave compound (III*a*) selectively. Reactions of the *p*-methyl, (I*b*), and *p*-chloro, (I*c*), derivatives of (*E*)-*o*-stilbenecarboxylic acid with the pyridine.HBr.Br_2 complex in the solid state also gave only compounds (III*b*) and (III*c*), respectively. However, the *p*-methoxy derivative, (I*d*), gave mainly compound (IV*d*).