Acta Cryst. (1998). C**54**, 1694–1695

A Bicyclic Cyclopropane Carboxylic Acid Lactone from a Solid–Liquid PTC Reaction

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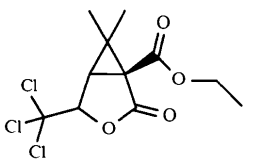
(*Received 10 November 1997; accepted 5 June 1998*)

Abstract

The structure of 6,6-dimethyl-4-trichloromethyl-3-oxa-bicyclo[3.1.0]hexan-2-one-1-carboxylic acid ethyl ester ($C_{11}H_{13}Cl_3O_4$), a potential pyrethroid-type intermediate, is presented. It is dominated by the interplanar angle [70.1 (3)°] formed by the lactone and the cyclopropane rings of the molecule. A structural comparison with other related published structures is also presented.

Comment

The reaction of non-activated olefines with CH-acids such as malonic acid, cyanoacetic acid or acetoacetic acid esters under solid–liquid phase-transfer conditions, in the presence of solid potassium carbonate as base, and iodine and a lipophilic quaternary ammonium salt as phase-transfer catalyst in toluene, results in cyclopropanecarboxylic acid derivatives (Tőke *et al.*, 1993). If the active methylene group is incorporated in the side chain of an olefine at a favourable position, *cis*-fused bicyclic cyclopropane carboxylic acid lactones can be obtained in an intramolecular cyclization with good yields. Some of these compounds are potential intermediates of the pyrethroid-type insecticides (Kondo *et al.*, 1980). In the literature we found the structures of four closely related compounds (Afonso *et al.*, 1982; Jones & Schrumpf, 1987; Mori *et al.*, 1983; Puranik, 1988). The bicycles in these structures assume the same conformation as in the title compound, (1). RMSD values after superposition of the bicycles of the four structures and that of (1) are all below 0.04 Å. Both the trichloromethyl and the ethoxycarbonyl substituents are positioned on the *exo* side of the lactone ring, since the other side is blocked by the dimethylcyclopropane moiety. Due to stereochemical restraints, out of the eight stereoisomers possible in a compound containing three chiral centres the PTC (phase-transfer catalysed) cyclization reaction used to prepare (1) allows only the production of the enantiomer pair present in the crystal structure due to stereochemical restraints.



(1)

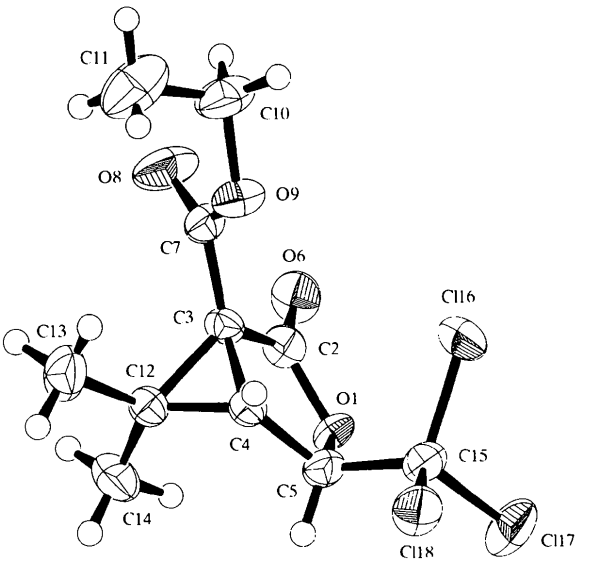


Fig. 1. Molecular structure and atomic numbering for (1). The displacement ellipsoids are drawn at the 50% probability level.

Experimental

The title compound was synthesized as described by Tőke *et al.* (1993).

Crystal data

$C_{11}H_{13}Cl_3O_4$
M_r = 315.56
Monoclinic
$P2_1/a$
a = 6.291 (2) Å
b = 11.009 (2) Å
c = 20.1850 (11) Å
β = 93.939 (11)°
V = 1394.7 (5) Å^3
Z = 4
D_x = 1.503 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 23 reflections
θ = 40.99–59.03°
μ = 6.004 mm^{-1}
T = 293 (2) K
Needle
0.400 × 0.150 × 0.150 mm
Transparent

Data collection

AFC-6*S* diffractometer
$\omega/2\theta$ scans

R_{int} = 0.047
θ_{max} = 75.18°

Absorption correction:	$h = -7 \rightarrow 7$
ψ scan (North *et al.*, 1968)	$k = -8 \rightarrow 13$
$T_{min} = 0.358$, $T_{max} = 0.406$	$l = -25 \rightarrow 25$
3044 measured reflections	3 standard reflections
2778 independent reflections	every 150 reflections
1588 reflections with $I > 2\sigma(I)$	intensity decay: 3.14%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.016$
$R[F^2 > 2\sigma(F^2)] = 0.059$	$\Delta\rho_{max} = 0.438$ e Å^{-3}
$wR(F^2) = 0.190$	$\Delta\rho_{min} = -0.328$ e Å^{-3}
$S = 1.088$	Extinction correction: *SHELXL*93
2770 reflections	Extinction coefficient: 0.0249 (14)
167 parameters	Scattering factors from *International Tables for Crystallography* (Vol. C)
Only H-atom U's refined	
$w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 2.8628P]$ where $P = (F_o^2 + 2F_c^2)/3$	

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

Cl16—C15	1.766 (6)	O6—C2	1.204 (6)
Cl17—C15	1.769 (5)	O8—C7	1.199 (6)
Cl18—C15	1.757 (6)	O9—C7	1.318 (7)
O1—C2	1.374 (6)	O9—C10	1.473 (7)
O1—C5	1.426 (6)		
C2—O1—C5	111.1 (4)	C12—C4—C3	62.3 (3)
O1—C2—C3	110.0 (4)	C3—C4—C5	105.6 (4)
C2—C3—C4	105.6 (4)	O1—C5—C4	106.9 (4)
C4—C3—C12	58.7 (3)	C4—C12—C3	59.0 (3)
O1—C2—C3—C12	−59.3 (6)	C7—O9—C10—C11	93.9 (7)
C12—C4—C5—O1	58.6 (6)	C2—C3—C12—C14	−18.5 (7)
C3—C4—C5—C15	110.8 (5)	C2—C3—C12—C13	−159.7 (5)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN*: *PROCESS* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Software used to prepare material for publication: *TEXSAN*: *FINISH*.

The authors are grateful to Chinoin Pharmaceuticals for supporting the project with manpower and instrumentation and wish to thank the OTKA Committee for financial support (T023046).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1266). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1695–1698

A Triclinic Modification of Triphenylphosphine

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(Received 28 April 1998; accepted 9 July 1998)

Abstract

A triclinic modification of triphenylphosphine, $C_{18}H_{15}P$, is reported. Two of the four unique molecules are in virtually the same conformation and are related by a local inversion centre; the other two molecules each have a different conformation. The structure contains a number of short C—H$\cdots\pi$ contacts.

Comment

The monoclinic modification of the title compound has been reported earlier by a number of authors (Daly, 1964; Dunne & Orpen, 1991; Chekhlov, 1993*a*,*b*; Bruckmann *et al.*, 1995).

In the triclinic modification reported here, the title compound, (I), crystallizes with four independent molecules in the asymmetric unit. As expected, the bond distances and angles of these four molecules display no significant differences from those observed in other determinations of the structure of triphenylphosphines, either in the monoclinic modification or cocrystallized with a variety of other molecules.