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(±)-(3a*R**,6*S**,7*S**,14a*R**)-2,3,3a,7,8,9,10,11,12,13,14,14a-Dodecahydro-1*H*,6*H*-3a,6-epoxy-7,14a-methanocyclopentacyclotridecen-15-one

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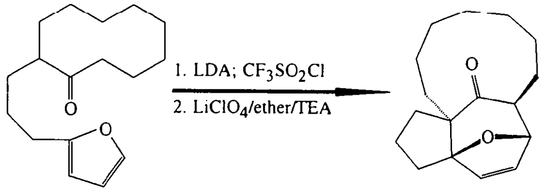
Abstract

The fused-ring system of the title compound, $C_{17}H_{24}O_2$, limits its conformational freedom. The five-membered cyclopentane and furan rings adopt envelope conformations, the tetrahydropyranone ring a boat conformation and the cyclodecanone ring a cyclodecane boat–chair–boat conformation.

Comment

As part of a continuing program involving the study of the intramolecular [4+3] cycloaddition reaction of allylic cations and dienes (Harmata, Gamlath, Barnes & Jones, 1995; Harmata, Elahmad & Barnes, 1994, 1995; Harmata & Herron, 1993*a*,*b*,*c*; Harmata & Elahmad, 1993; Harmata & Gamlath, 1988; Harmata, Gamlath & Barnes, 1990, 1993; Harmata, Fletcher & Claassen, 1991), we had occasion to study the reaction of the oxyallylic species generated from ketone (I) *via* chlorination and oxyallyl generation under conditions introduced by Föhlisch (Harmata, Elahmad & Barnes, 1995; Kaiser & Föhlisch, 1990, and references therein). The cycloaddition products were isolated as a 19:1 mixture in 59% yield. The major product (II) was isolated, crystallized from hexanes and its structure determined.



(I) (II)

Most interesting is the conformation of the tetrahydropyranone portion of the molecule, which is a boat with the methylene chain derived from cyclodecanone occupying both axial and equatorial positions at the 2 and 6 positions of the tetrahydropyranone. Vinter & Hoffman (1974) speculated that a minor product in the intermolecular [4+3] cycloaddition of cyclodecenyl oxyallyl to furan possessed this structure. Our isolation and structure determination of (II) supports their conjecture and their conclusion that cyclodecenyl oxyallylic cations are sickle shaped.

The bond lengths and angles fall within expected limits. The boat conformation of the tetrahydropyran-

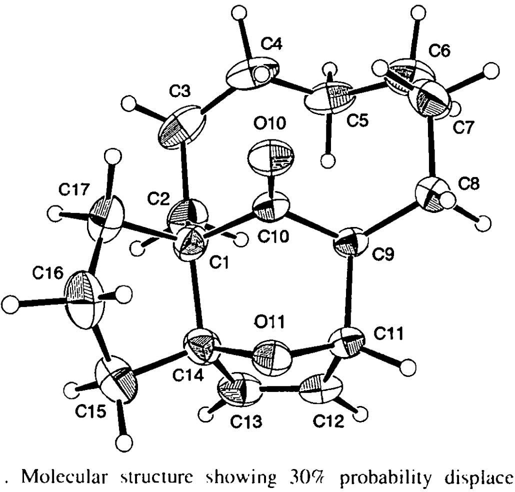


Fig. 1. Molecular structure showing 30% probability displacement ellipsoids.

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one ring is somewhat flattened at C10 [C1—C10—C9 = 113.9 (2)°] and compressed at O11 [C11—O11—C14 = 102.53 (14)°]. It is also slightly twisted [C10—C9—C11—O11 = −4.6 (2) and C10—C1—C14—O11 = 13.4 (2)°]. This distortion communicates to the cyclopentane ring composed of C1, C14, C15, C16 and C17, which is a slightly twisted envelope with C16 at the flap [C17—C1—C14—C15 = 11.5 (3)°]. The furan ring is an envelope with O11 at the flap. Examination of the structure with Dreiding models suggests that the constraints of this fused-ring core limit the conformational freedom of the cyclodecanone ring, which assumes the boat–chair conformation.

Experimental

The title compound was prepared as described above and crystallized from hexanes.

Crystal data

$C_{17}H_{24}O_2$
$M_r = 260.37$
Monoclinic
$C2/c$
$a = 31.208\ (2)$ Å
$b = 8.7588\ (4)$ Å
$c = 10.9435\ (11)$ Å
$\beta = 101.706\ (3)°$
$V = 2929.1\ (4)$ Å^3
$Z = 8$
$D_x = 1.181$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 20–25°$
$\mu = 0.56$ mm^{-1}
$T = 298$ K
Rod
0.45 × 0.20 × 0.20 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2306 measured reflections
2169 independent reflections
1922 observed reflections [$I > 2.5\sigma(I)$]

$R_{\rm int} = 0.023$
$\theta_{\rm max} = 60°$
$h = -34 \rightarrow 34$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 12$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F
$R = 0.054$
$wR = 0.090$
$S = 3.18$
1922 reflections
173 parameters
H atoms riding
$w = 1/[\sigma^2(F) + 0.0005F^2]$
$(\Delta/\sigma)_{\rm max} = 0.003$

$\Delta\rho_{\rm max} = 0.40$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 2.4 (3)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{\rm eq} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
O10	0.13098 (5)	0.0533 (2)	0.27729 (13)	4.85 (8)
O11	0.04541 (4)	0.1017 (3)	0.10242 (13)	3.95 (6)
C1	0.11355 (8)	0.2439 (2)	0.1165 (2)	4.36 (9)
C2	0.14303 (8)	0.2806 (3)	0.0230 (3)	5.73 (12)
C3	0.19331 (10)	0.2757 (4)	0.0795 (3)	7.5 (2)
C4	0.21278 (8)	0.1218 (4)	0.1277 (3)	6.6 (2)
C5	0.20764 (7)	−0.0076 (4)	0.0329 (3)	6.4 (2)
C6	0.20459 (9)	−0.1720 (4)	0.0786 (3)	7.4 (2)
C7	0.17361 (9)	−0.2134 (3)	0.1609 (3)	6.64 (14)
C8	0.12430 (7)	−0.1994 (3)	0.1120 (2)	4.70 (10)
C9	0.10892 (6)	−0.0402 (2)	0.0677 (2)	3.51 (8)
C10	0.12085 (6)	0.0820 (2)	0.1666 (2)	3.53 (9)
C11	0.05824 (6)	−0.0153 (2)	0.0236 (2)	3.71 (9)
C12	0.04848 (7)	0.0608 (3)	−0.1022 (2)	4.59 (11)
C13	0.05123 (7)	0.2091 (3)	−0.0828 (2)	5.12 (11)
C14	0.06193 (7)	0.2394 (2)	0.0555 (2)	4.39 (10)
C15	0.04279 (11)	0.3741 (3)	0.1112 (3)	7.1 (2)
C16	0.07088 (13)	0.3852 (4)	0.2433 (4)	8.1 (2)
C17	0.11743 (10)	0.3623 (3)	0.2227 (3)	6.64 (14)

Table 2. *Selected geometric parameters (°)*

C11—O11—C14	102.53 (14)	C1—C10—C9	113.9 (2)
C14—O11—C11—C9	74.5 (3)	C1—C2—C3—C4	64.0 (4)
C11—O11—C14—C1	−79.7 (3)	C2—C3—C4—C5	59.1 (4)
C14—C1—C10—C9	58.5 (2)	C3—C4—C5—C6	−150.1 (6)
C10—C1—C14—O11	13.4 (2)	C4—C5—C6—C7	49.6 (4)
C11—C9—C10—C1	−64.0 (3)	C5—C6—C7—C8	64.4 (4)
C10—C9—C11—O11	−4.6 (2)	C6—C7—C8—C9	−57.7 (3)
C14—O11—C11—C12	−41.3 (2)	C7—C8—C9—C10	−57.6 (3)
C11—O11—C14—C13	40.2 (2)	C8—C9—C10—C1	168.7 (4)
O11—C11—C12—C13	26.4 (2)	C17—C1—C14—C15	11.5 (3)
C11—C12—C13—C14	−1.2 (2)	C14—C1—C17—C16	15.2 (3)
C12—C13—C14—O11	−24.5 (2)	C1—C14—C15—C16	−33.6 (3)
C10—C1—C2—C3	−62.8 (3)	C14—C15—C16—C17	43.8 (3)
C2—C1—C10—C9	−63.3 (3)	C15—C16—C17—C1	−36.2 (3)

H atoms were placed at calculated positions and included using a riding model, each with a fixed isotropic displacement parameter equal to 1.3 times that of the attached atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX*. Program(s) used to refine structure: *NRCVAX*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *NRCVAX*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1040). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3,5-Dichloro-2,6-dimethoxycyclohexa-2,5-diene-1,4-dione

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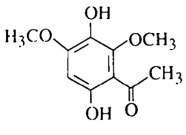
Abstract

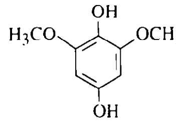
A new synthesis of the title compound, $C_8H_6Cl_2O_4$, is described. The molecule has a mirror plane and the six-membered carbon ring assumes a slight boat conformation. The ring substituents are arranged in an alternating 'up and down' pattern with respect to the best plane through the ring C atoms.

Comment

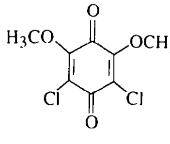
Dichlorodimethoxycyclohexadiene-1,4-diones are reported to possess bacteriostatic activity against gram positive bacteria (Hayashi, 1954) and they are also good synthons in different types of Diels–Alder (Mehta, Srikrishna, Veera Reddy & Nair, 1981) and 1,3-dipolar cycloaddition reactions (Shiraishi, Ikeuchi, Seno & Asahara, 1978). The preparation of a useful synthon, 3,6-dihydroxy-2,4-dimethoxyacetophenone, (I), for the preparation of a range of chalcones and other flavonoids, was attempted *via* the acylation of 1,4-dihydroxy-2,6-dimethoxybenzene, (II), using the Hoesch reaction (Norman, 1978). The reaction failed to produce compound (I), but instead gave 3,5-dichloro-2,6-dimethoxycyclohexa-2,5-diene-1,4-dione, (III). Compound (III) has been synthesized previously by two different methods (Lindberg, 1953; Davidge, Davies, Kenyon & Mason, 1958), but its spectral and structural characteristics have not been reported. We obtained (III) in the form of bright orange crystals. The X-ray structure and other spectral data reported here were determined in order to assign its constitution unambiguously.



(I)



(II)



(III)

The molecular structure of (III) is represented in Fig. 1. The ring is bisected by a mirror plane passing through O1, C1, C4 and O3. The C1—O1 and C4—O3 bond lengths are the same within experimental error, and are consistent with double bonding. The C2—C3 bond length of 1.340 (2) Å is also indicative of double bonding. All of the bond lengths and angles are unexceptional.

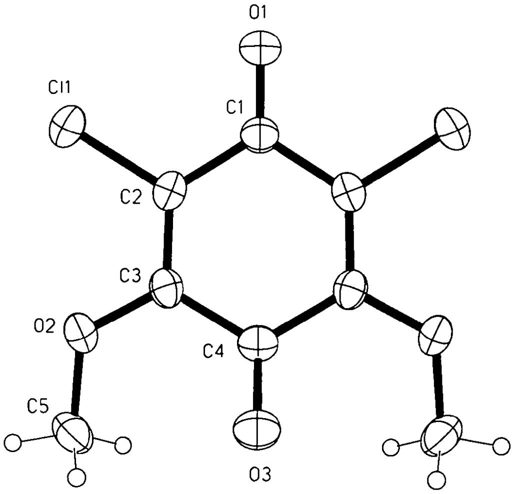


Fig. 1. View of the molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

The six-membered carbon ring has a slight boat conformation; this contrasts with that of unsubstituted 2,5-cyclohexadiene-1,4-dione which has a chair conformation (van Bolhuis & Kiers, 1978). Deviations from the best least-squares plane through the six C atoms in the ring are: C1 0.063 (2), C2, C2*a* −0.021 (1), C3, C3*a*

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