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

C(4)—Br	1.874 (2)	C(13)—N(4)	1.351 (3)
O(1)—S(1)	1.415 (2)	C(14)—N(4)	1.317 (3)
O(2)—S(1)	1.441 (2)	C(14)—N(5)	1.338 (4)
N(1)—S(1)	1.624 (2)	C(14)—N(6)	1.350 (4)
C(1)—S(1)	1.753 (2)	C(2)—C(1)	1.381 (4)
C(9)—S(2)	1.802 (4)	C(6)—C(1)	1.382 (3)
C(10)—S(2)	1.808 (3)	C(3)—C(2)	1.369 (4)
C(12)—S(3)	1.678 (3)	C(4)—C(3)	1.396 (4)
C(13)—S(3)	1.740 (2)	C(5)—C(4)	1.369 (4)
C(7)—N(1)	1.326 (3)	C(6)—C(5)	1.400 (4)
C(7)—N(2)	1.319 (3)	C(9)—C(8)	1.522 (4)
C(8)—N(2)	1.446 (3)	C(11)—C(10)	1.496 (4)
C(11)—N(3)	1.380 (3)	C(12)—C(11)	1.354 (4)
C(13)—N(3)	1.313 (3)		
O(2)—S(1)—O(1)	118.7 (1)	C(5)—C(4)—Br	119.0 (2)
N(1)—S(1)—O(1)	104.5 (1)	C(5)—C(4)—C(3)	120.7 (2)
N(1)—S(1)—O(2)	111.7 (1)	C(6)—C(5)—C(4)	119.7 (2)
C(1)—S(1)—O(1)	107.4 (1)	C(5)—C(6)—C(1)	119.1 (3)
C(1)—S(1)—O(2)	107.3 (1)	N(2)—C(7)—N(1)	121.0 (2)
C(1)—S(1)—N(1)	106.4 (1)	C(9)—C(8)—N(2)	113.3 (2)
C(10)—S(2)—C(9)	103.5 (2)	C(8)—C(9)—S(2)	114.8 (2)
C(13)—S(3)—C(12)	90.5 (1)	C(11)—C(10)—S(2)	114.5 (2)
C(7)—N(1)—S(1)	116.8 (2)	C(10)—C(11)—N(3)	119.4 (3)
C(8)—N(2)—C(7)	123.1 (3)	C(12)—C(11)—N(3)	115.4 (3)
C(13)—N(3)—C(11)	110.8 (2)	C(12)—C(11)—C(10)	125.1 (3)
C(14)—N(4)—C(13)	121.5 (2)	C(11)—C(12)—S(3)	110.5 (2)
C(2)—C(1)—S(1)	120.0 (2)	N(3)—C(13)—S(3)	112.8 (2)
C(6)—C(1)—S(1)	119.1 (2)	N(4)—C(13)—S(3)	117.2 (2)
C(6)—C(1)—C(2)	120.8 (2)	N(4)—C(13)—N(3)	129.9 (2)
C(3)—C(2)—C(1)	120.1 (2)	N(5)—C(14)—N(4)	117.2 (3)
C(4)—C(3)—C(2)	119.6 (2)	N(6)—C(14)—N(4)	125.2 (3)
C(3)—C(4)—Br	120.3 (2)	N(6)—C(14)—N(5)	117.6 (3)

Of the H atoms, 15 were found in the difference synthesis and two were computed. All were refined with an overall temperature factor, a riding model being used for the computed atoms.

The *CFEO* program (Solans, 1978) was used for data reduction. The structure was determined by direct methods using *SHELXS*86 (Sheldrick, 1990) and refined by full-matrix least squares with *SHELX*76 (Sheldrick, 1976). The molecular view was obtained using a PC version of *ORTEP* (Brueggemann & Schmid, 1990).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates and geometry have been deposited with the IUCr (Reference: NA1081). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Anglada, Ll., Márquez, M., Sacristán, A. & Ortiz, J. A. (1988). *Eur. J. Med. Chem.* **23**, 97–100.

Brueggemann, R. & Schmid, G. (1990). PC version of *ORTEP*3.2 and *PLUTO*4.1. Univ. of Ulm, Germany.

Golic, L., Djinovic, K. & Florjanic, M. (1989). *Acta Cryst.* C**45**, 1381–1384.

Hadicke, E., Fickel, F. & Franke, A. (1978). *Chem. Ber.* **111**, 3222–3232.

Ishida, T., In, Y., Doi, M., Inoue, M. & Yanagisawa, I. (1989). *Acta Cryst.* B**45**, 505–512.

Kojic-Prodic, B., Ruzic-Toros, Z., Bresciani-Pahor, N. & Randaccio, L. (1980). *Acta Cryst.* B**36**, 1223–1225.

Kojic-Prodic, B., Ruzic-Toros, Z. & Toso, R. (1982). *Acta Cryst.* B**38**, 1837–1840.

Sheldrick, G. M. (1976). *SHELX*76. *Program for Crystal Structure Determination*. Univ. of Cambridge, England.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Solans, X. (1978). *CFEO*. Univ. of Barcelona, Spain.

Solans, X., Font-Altaba, M. & Cuevas-Diarte, M. A. (1988). *Z. Kristallogr.* **185**, 147.

Solans, X., Font-Altaba, M. & Cuevas-Diarte, M. A. (1995). *Acta Cryst.* Submitted.

Yanagisawa, I., Hirata, Y. & Ishii, Y. (1987). *J. Med. Chem.* **30**, 1787–1793.

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The Diels–Alder Reaction Product of β-Ionone and Maleic Anhydride

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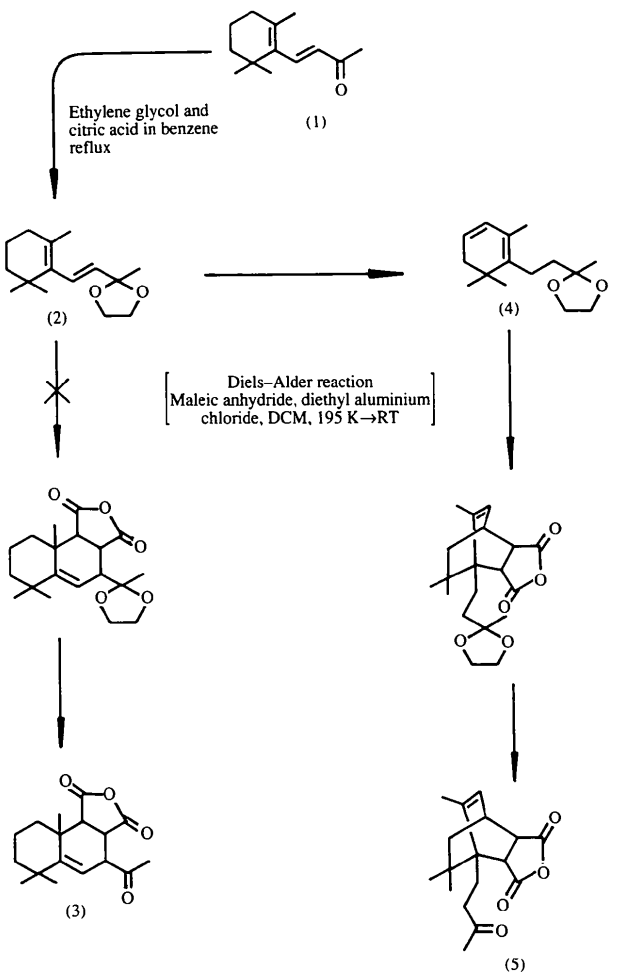
Abstract

The structure of the title compound, 6,7,7-trimethyl-1-(3-oxobutyl)bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic acid anhydride, $C_{17}H_{22}O_4$, a Diels–Alder reaction product of β-ionone and maleic anhydride, was solved by direct methods. The three six-membered rings of the bicyclo[2.2.2]oct-5-ene cage all slightly deviate from ideal boat conformations. The 3-oxobutyl side chain has an extended configuration.

Comment

Several drimanic terpenes, like polygodial and warburganal, are very active insect antifeedents (Kubo, Lee, Pettei, Pilkiewicz & Nakanishi, 1976). In an effort to synthesize them from freely available β-ionone (1), a Diels–Alder reaction was envisaged with maleic anhydride. Since the carbonyl deactivates the diene it was thought to be protected as an ethylene ketal (2) [^{1}H NMR ($CDCl_3$): δ 0.95 (*s*, 6H, 2 × CH_3), 1.35–1.60 (*m*, 7H, 2 × CH_2 and CH_3), 1.65 (*s*, 3H, C=C—CH_3), 1.97 (*t*, 2H, C=C—CH_2, *J* = 6.0 Hz), 3.90–4.00 (*m*, 4H, 2 × CH_2—O), 5.20 (*d*, 1H, olefinic, *J* = 16.0 Hz), 6.14 (*d*, 1H, olefinic, *J* = 16.0 Hz)] and then subjected to Diels–Alder reaction. The ^{1}H NMR spectrum of the product, which had the molecular formula $C_{17}H_{22}O_4$, corresponding to the anticipated product (3), did not, however, have signals for a tertiary methyl at a ring junction, but instead had an sp^2-methyl proton signal at

1.78 p.p.m. This led to the proposal of structure (5), but in view of its novelty an X-ray crystal structure analysis was undertaken.



The crystal structure determination establishes the structure and the overall conformation in the solid state (Fig. 1). The bond distances and angles are in the normal range. The two C_{sp^3}—C_{sp^3} bonds [C5—C6 1.596 (6) and C6—C7 1.571 (5) Å], involving the bridgehead C6 atom, are, however, significantly larger than the average value of 1.541 Å of the other C_{sp^3}—C_{sp^3} bonds in the structure. This lengthening, probably associated with internal strain in the molecule, has been observed previously in similar crystal structures (Karlsson, Pilotti & Wiehager, 1973; Alex, Srinivasan, Bakthavatchalam, Ramadas & Varghese, 1993; Jerzykiewicz, Dziewonska-Baran, Baran & Lis, 1993). Furthermore, the presence of the C17 methyl group attached to C9, which is in a *cis* position relative to C11 [C11—C6—C9—C17 4.58 (5)° and C11···C17 2.98 (7) Å] may have also contributed to the lengthening of C6—C7 and C5—C6 bonds.

The bicyclo[2.2.2]oct-5-ene cage consists of three six-membered rings which all adopt distorted boat conformations with varying degrees of distortion, quantified by the asymmetry parameters ΔC_s (Duax & Norton, 1975) at their flagpole atoms: 5.6° at C3, 1.6° at C4 and 7.3° at C10. The 3-oxobutyl side chain has an extended configuration [C6—C11—C12—C13 173.3 (4)°]. The molecules in the crystal are bound by intermolecular van der Waals forces.

The formation of (5) can be rationalized by the cycloaddition reaction between maleic anhydride and (2) through the intermediate (4) [obtained by the migration of the double bonds in (2)] under the reaction condition where diethyl aluminium chloride has been used as catalyst.

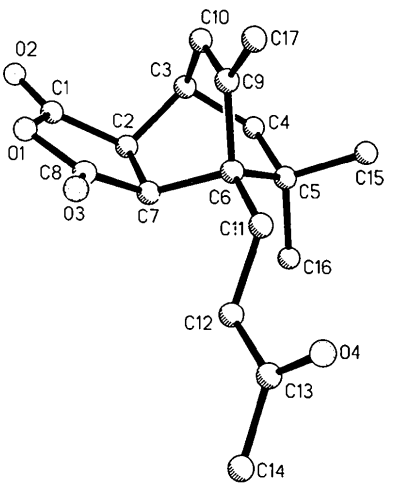


Fig. 1. A perspective view of the molecule with atom labelling. H atoms are omitted for clarity.

Experimental

A mixture of β-ionone (5 g, 26 mmol), ethylene glycol (2.2 g, 52 mmol) and citric acid (100 mg) in dry benzene (100 ml) was refluxed with removal of water formed using a Deen–Stark apparatus. The reaction mixture was cooled, washed with 10% aqueous $NaHCO_3$, and dried to obtain the ketal (2). This ketal, when subjected to Diels–Alder reaction (maleic anhydride and diethyl aluminium chloride in dichloromethane, at 195 K → room temperature), gave the product (5). (See reaction scheme.) Recrystallization from methanol resulted in diffraction-grade crystals.

Crystal data

$C_{17}H_{22}O_4$	Mo $K\alpha$ radiation
M_r = 290.36	λ = 0.71073 Å
Orthorhombic	Cell parameters from 25 reflections
$P2_12_12_1$	θ = 11–26°
a = 9.240 (2) Å	μ = 0.09 mm^{-1}
b = 10.761 (2) Å	T = 293 K
c = 15.217 (3) Å	Needle
V = 1513.1 (5) $Å^3$	0.18 × 0.15 × 0.14 mm
Z = 4	Colorless
D_x = 1.275 Mg m^{-3}	

Data collection

Siemens *R3m/V* diffractometer	$\theta_{max} = 22.5°$
$\omega/2\theta$ scans	$h = 0 \rightarrow 9$
Absorption correction: none	$k = 0 \rightarrow 11$
1187 measured reflections	$l = 0 \rightarrow 16$
1169 independent reflections	2 standard reflections monitored every 98 reflections
968 observed reflections $[I > 3\sigma(I)]$	intensity decay: $\leq 1\%$

Refinement

Refinement on F	$(\Delta/\sigma)_{max} < 0.001$
$R = 0.039$	$\Delta\rho_{max} = 0.12$ e Å^{-3}
$wR = 0.045$	$\Delta\rho_{min} = -0.15$ e Å^{-3}
$S = 0.884$	Extinction correction: none
968 reflections	Atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1990)
190 parameters	
$w = 1/[\sigma^2(F) + 0.0029F^2]$	

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

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
O1	0.1243 (4)	0.3408 (3)	0.9304 (2)	0.060 (1)
O2	0.3264 (5)	0.2471 (3)	0.8864 (2)	0.091 (1)
O3	−0.0349 (4)	0.4661 (3)	0.9967 (2)	0.071 (1)
O4	−0.1278 (4)	0.7074 (4)	1.2510 (3)	0.099 (2)
C1	0.2646 (6)	0.3049 (4)	0.9427 (3)	0.057 (2)
C2	0.3208 (5)	0.3481 (4)	1.0303 (3)	0.046 (1)
C3	0.4462 (4)	0.4424 (4)	1.0201 (3)	0.049 (1)
C4	0.4958 (5)	0.4769 (4)	1.1129 (3)	0.053 (1)
C5	0.3719 (4)	0.5398 (4)	1.1654 (3)	0.042 (1)
C6	0.2315 (4)	0.5479 (3)	1.1046 (2)	0.038 (1)
C7	0.1918 (4)	0.4132 (3)	1.0729 (2)	0.039 (1)
C8	0.0801 (5)	0.4143 (4)	1.0011 (3)	0.048 (1)
C9	0.2807 (4)	0.6141 (3)	1.0197 (2)	0.040 (1)
C10	0.3858 (5)	0.5585 (4)	0.9774 (3)	0.047 (1)
C11	0.1000 (4)	0.6109 (4)	1.1503 (3)	0.046 (1)
C12	0.0009 (5)	0.5282 (4)	1.2048 (3)	0.053 (1)
C13	−0.1124 (5)	0.5940 (5)	1.2550 (3)	0.051 (1)
C14	−0.2110 (5)	0.5160 (5)	1.3100 (3)	0.068 (2)
C15	0.4193 (5)	0.6706 (4)	1.1928 (3)	0.055 (1)
C16	0.3445 (5)	0.4635 (4)	1.2511 (2)	0.054 (1)
C17	0.2136 (6)	0.7344 (4)	0.9887 (3)	0.061 (1)

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

C2—C3	1.548 (6)	C2—C7	1.526 (6)
C3—C4	1.529 (6)	C3—C10	1.514 (6)
C4—C5	1.552 (6)	C5—C6	1.596 (6)
C6—C7	1.571 (5)	C6—C9	1.544 (5)
C9—C10	1.310 (6)		
C3—C2—C7	109.0 (3)	C2—C3—C10	107.9 (3)
C2—C3—C4	106.9 (3)	C4—C3—C10	107.8 (3)
C3—C4—C5	111.1 (3)	C4—C5—C6	108.9 (3)
C5—C6—C9	105.8 (3)	C5—C6—C7	108.5 (3)
C7—C6—C9	103.7 (3)	C2—C7—C6	111.8 (3)
C6—C9—C10	114.7 (3)	C3—C10—C9	116.1 (4)

H atoms were located from difference Fourier maps; they were positioned geometrically and included as riding atoms with fixed isotropic temperature factors in the structure-factor calculations.

Data collection: *Siemens P3 Diffractometer Program* (Siemens, 1989). Cell refinement: *Siemens P3 Diffractometer Program*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1990). Structure solution: *SHELXTL-Plus*. Structure refinement: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Preparation of materials for publication: *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: VJ1007). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Alex, G., Srinivasan, S., Bakthavatchalam, R., Ramadas, S. R. & Varghese, B. (1993). *Acta Cryst.* C**49**, 303–307.

Duax, W. L. & Norton, D. A. (1975). *Atlas of Steroid Structure*, Vol. 1. New York: Plenum.

Jerzykiewicz, L. B., Dziewonska-Baran, D., Baran, J. & Lis, T. (1993). *Acta Cryst.* C**49**, 400–402.

Karlsson, B., Pilotti, A. M. & Wiehager, A. C. (1973). *Acta Chem. Scand.* **27**, 2955–2964.

Kubo, I., Lee, Y. W., Pettei, M., Pilkiewicz, F. & Nakanishi, K. (1976). *J. Chem. Soc. Chem. Commun.* pp. 1013–1014.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Sheldrick, G. M. (1990). *SHELXTL-Plus*, Revision 4.11. Siemens Analytical X-ray Instruments, Karlsruhe, Germany.

Siemens (1989). *P3 Diffractometer Program*. Version 4.21. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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Structural Studies of Intermediates in the Synthesis of Mifepristone (RU 486). II. Structure of a β-Epoxy Steroid

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Abstract

Structure determination of the title compound, 5β,10-β-epoxy-3,3-ethylenedioxy-17β-hydroxy-17α-(1-propynyl)estra-9 (11)-ene, $C_{23}H_{30}O_4$, establishes the configuration of the epoxy O atom as 5β,10β and locates the position of the double bond between C(9) and C(11). The strain caused by the presence of an epoxy O atom between C(5) and C(10) in the molecule is reflected in the distortion of bond angles around several tetrahedral