

Vater, W., Kroneberg, G., Hoffmeister, F., Kaller, H., Meng, K., Oberdorf, A., Puls, W., Schloßmann, K. & Stopel, K. (1972). *Arzneim.-Forsch.* **22**, 1–14.
 Waldman, S. A. & Murad, F. (1988). *J. Cardiovasc. Pharmacol.* **12** (Suppl. 5), S115–S118.

Acta Cryst. (1993). **C49**, 996–998

Structure of the Epoxide of a Tricyclic Lactone

JOEL T. MAGUE,* HARRY E. ENSLEY AND GUOQING CHEN

Department of Chemistry, Tulane University, New Orleans, Louisiana 70118, USA

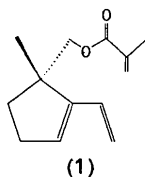
(Received 10 July 1992; accepted 16 November 1992)

Abstract

The crystal structure of 1,5-dimethyl-3,9-dioxatetracyclo[8.3.0.0^{5,11}.0^{8,10}]tridecan-4-one, (4), obtained from the epoxidation of the olefin generated by the intramolecular Diels–Alder reaction of the methacrylate ester of 3-hydroxymethyl-3-methyl-2-vinylcyclopentene, demonstrates that the desired regioselectivity in the cycloaddition reaction has occurred. The five-membered carbocyclic ring is distinctly non-planar and there is significant strain in the portion of the lactone adjacent to this ring and at the junction with the six-membered ring adjacent to the epoxide moiety.

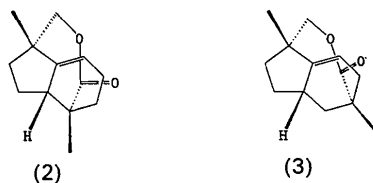
Comment

In connection with model studies directed towards the synthesis of cinnassiol D₁ (Nohara *et al.*, 1980, 1981) we were interested in the regioselectivity of the intramolecular Diels–Alder reaction of (1).

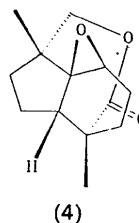


Previous work on related systems (Shea *et al.*, 1982; Shea, Lease & Ziller, 1990; Shea, Staab & Zandi, 1991) indicated that the length of the 'tether' between the 2-position of the diene and the dienophile influences the regioselectivity, with a five-atom tether preferentially giving the 'meta' adduct (Shea *et al.*, 1991). Compound (1) has a four-atom

tether and while a single low-melting product was obtained from its intramolecular cycloaddition, NMR could not distinguish between the desired 'meta' isomer (2) and the 'para' isomer (3) because of an accidental chemical-shift degeneracy of the allylic



methine and methylene resonances. As suitable crystals of the product olefin could not be obtained, it was epoxidized to yield a single product, (4), which formed X-ray quality crystals when a concentrated ethanol solution was cooled at 278 K. The structure of (4) (Fig. 1) confirms that the product of the intramolecular cycloaddition is indeed the 'meta' isomer (2).



Compound (4) crystallizes as a racemic mixture with no unusual intermolecular contacts. The five-membered ring is distinctly non-planar with C(2) lying nearly in the weighted least-squares plane and the remaining four atoms 0.138 (2)–0.202 (3) Å from it. Most bond distances and interbond angles are

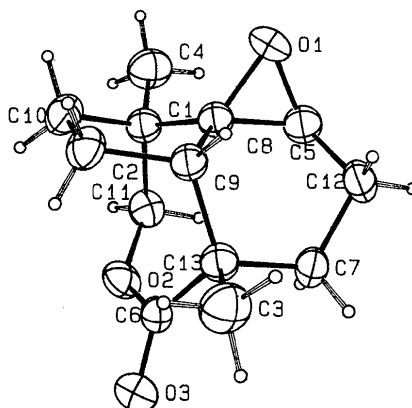


Fig. 1. A perspective view of (4). Thermal ellipsoids for non-H atoms are drawn at the 40% probability level. H atoms are drawn artificially small for clarity and are numbered to correspond to the attached C atoms.

normal with the exception of the angles C(6)—O(2)—C(11), O(2)—C(11)—C(1) and C(1)—C(8)—C(5) which are considerably larger than ideal. These indicate that there is significant strain in the lactone moiety and in the junction of the two carbocyclic rings adjacent to the epoxide.

Experimental

Crystal data

$C_{13}H_{18}O_3$
 $M_r = 222.29$
 Orthorhombic
 $Pca2_1$
 $a = 11.562(2) \text{ \AA}$
 $b = 9.9784(9) \text{ \AA}$
 $c = 9.6781(9) \text{ \AA}$
 $V = 1116.6(4) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.322 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$

Data collection

Enraf-Nonius CAD-4 diffractometer
 ω - 2θ scans
 Absorption correction: none
 1434 measured reflections
 1434 independent reflections
 851 observed reflections
 $[I \geq 2.0\sigma(I)]$

Refinement

Refinement on F
 Final $R = 0.039$
 $wR = 0.048$
 $S = 1.53$
 851 reflections
 127 parameters
 $w = 4F/[(\sigma_I)^2 + (0.04F^2)^2]$
 $(\Delta/\sigma)_{\max} = 0.06$

Cell parameters from 25 reflections

$\theta = 13.20$ – 17.83°
 $\mu = 0.086 \text{ mm}^{-1}$
 $T = 296 \text{ K}$

Rectangular plate
 $0.40 \times 0.40 \times 0.17 \text{ mm}$
 Colorless

Crystal source: from concentrated ethanol solution at 278 K

$\theta_{\max} = 27^\circ$
 $h = 0 \rightarrow 14$
 $k = 0 \rightarrow 12$
 $l = 0 \rightarrow 12$
 3 standard reflections
 frequency: 120 min
 intensity variation: -7.6% over 13.4 h

$\Delta\rho_{\max} = 0.16 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.22 \text{ e \AA}^{-3}$
 Extinction coefficient: $I_c/I_o = 0.974 + (2.9 \times 10^{-7} I_c)$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters (\AA^2)

An asterisk denotes an isotropically refined atom; for the other atoms $B_{\text{eq}} = (8\pi^2/3)(U_{11} + U_{22} + U_{33})$.

	x	y	z	$B_{\text{iso}}/B_{\text{eq}}$
O(1)	0.1220 (2)	0.1272 (2)	-0.186	4.66 (5)
O(2)	-0.1431 (2)	0.3952 (2)	0.0178 (3)	3.83 (4)
O(3)	-0.1242 (2)	0.4110 (3)	0.2387 (3)	4.85 (5)
C(1)	-0.0792 (3)	0.2437 (3)	-0.1803 (4)	3.31 (6)*
C(2)	-0.1234 (3)	0.0965 (3)	0.0154 (4)	3.88 (7)
C(3)	0.0295 (4)	0.2067 (4)	0.2780 (4)	4.98 (9)
C(4)	-0.0728 (4)	0.2546 (4)	-0.3377 (4)	5.11 (9)
C(5)	0.1440 (3)	0.2599 (3)	-0.1315 (4)	3.76 (6)*
C(6)	-0.0869 (3)	0.3614 (3)	0.1343 (4)	3.15 (6)
C(7)	0.1270 (3)	0.3512 (3)	0.0988 (4)	3.75 (7)
C(8)	0.0310 (3)	0.1995 (3)	-0.1127 (4)	3.09 (5)*
C(9)	0.0006 (3)	0.1506 (3)	0.0283 (4)	3.07 (5)*
C(10)	-0.1693 (3)	0.1431 (3)	-0.1256 (5)	4.08 (7)

C(11)	-0.1052 (3)	0.3844 (3)	-0.1260 (4)	3.49 (6)
C(12)	0.2092 (3)	0.2797 (4)	0.0006 (4)	4.15 (8)
C(13)	0.0163 (3)	0.2667 (3)	0.1347 (4)	3.30 (6)*
H(5)	0.151 (2)	0.318 (3)	-0.198 (3)	1.6 (5)*
H(9)	0.060 (3)	0.079 (3)	0.058 (3)	3.6 (7)*

Table 2. Geometric parameters (\AA , $^\circ$)

O(1)—C(5)	1.450 (6)	C(3)—C(13)	1.513 (7)
O(1)—C(8)	1.467 (6)	C(5)—C(8)	1.453 (7)
O(2)—C(6)	1.343 (6)	C(5)—C(12)	1.497 (8)
O(2)—C(11)	1.464 (7)	C(5)—H(5)	0.76 (5)
O(3)—C(6)	1.207 (6)	C(6)—C(13)	1.521 (6)
C(1)—C(4)	1.534 (7)	C(7)—C(12)	1.521 (7)
C(1)—C(8)	1.495 (6)	C(7)—C(13)	1.569 (6)
C(1)—C(10)	1.543 (7)	C(8)—C(9)	1.494 (7)
C(1)—C(11)	1.522 (6)	C(9)—C(13)	1.564 (6)
C(2)—C(9)	1.541 (6)	C(9)—H(9)	0.98 (5)
C(2)—C(10)	1.545 (8)		
C(5)—O(1)—C(8)	59.8 (3)	O(1)—C(8)—C(5)	59.5 (3)
C(6)—O(2)—C(11)	129.3 (3)	O(1)—C(8)—C(9)	116.9 (4)
C(4)—C(1)—C(8)	114.4 (4)	C(1)—C(8)—C(5)	126.6 (4)
C(4)—C(1)—C(10)	115.1 (4)	C(1)—C(8)—C(9)	107.1 (4)
C(4)—C(1)—C(11)	106.6 (4)	C(5)—C(8)—C(9)	117.2 (4)
C(8)—C(1)—C(10)	103.4 (4)	C(2)—C(9)—C(8)	105.7 (4)
C(8)—C(1)—C(11)	106.6 (4)	C(2)—C(9)—C(13)	114.9 (4)
C(10)—C(1)—C(11)	110.5 (4)	C(2)—C(9)—H(9)	108. (3)
C(9)—C(2)—C(10)	105.8 (4)	C(8)—C(9)—C(13)	109.3 (4)
O(1)—C(5)—C(8)	60.7 (3)	C(8)—C(9)—H(9)	116. (3)
O(1)—C(5)—C(12)	122.0 (4)	C(13)—C(9)—H(9)	103. (3)
O(1)—C(5)—H(5)	108. (3)	C(1)—C(10)—C(2)	106.0 (4)
C(8)—C(5)—C(12)	114.1 (5)	O(2)—C(11)—C(1)	117.0 (4)
C(8)—C(5)—H(5)	116. (3)	C(5)—C(12)—C(7)	106.0 (4)
C(12)—C(5)—H(5)	121. (3)	C(3)—C(13)—C(6)	108.8 (4)
O(2)—C(6)—O(3)	115.2 (4)	C(3)—C(13)—C(7)	110.1 (4)
O(2)—C(6)—C(13)	122.7 (4)	C(3)—C(13)—C(9)	108.6 (4)
O(3)—C(6)—C(13)	122.2 (5)	C(6)—C(13)—C(7)	107.7 (3)
C(12)—C(7)—C(13)	113.3 (4)	C(6)—C(13)—C(9)	111.0 (4)
O(1)—C(8)—C(1)	123.1 (4)	C(7)—C(13)—C(9)	110.5 (4)

Crystal orientation, unit-cell determination and refinement, data collection: CAD-4 Version 5.0 (Schagen, Staver, van Meurs & Williams, 1989). Data reduction and structure refinement: *MolEN* (Enraf-Nonius, 1990). Structure solution: *MULTAN80* (Main *et al.*, 1980). Graphics: *ORTEPII* (Johnson, 1976). Refinement was by the full-matrix least-squares method. Because of the limited number of data not all non-H atoms could be refined anisotropically. The bridgehead atoms [C(1), C(5), C(8), C(9) and C(13)] were refined isotropically as it was considered these should be constrained most. For the same reason, although all H atoms were clearly visible in difference maps, only those attached to the bridgehead atoms [H(5) on C(5) and H(9) on C(9)] were refined because possible ring strain about these atoms could make it unrealistic to define idealized positions. All methyl and methylene H atoms were placed in calculated positions with C—H = 0.95 \AA and isotropic thermal parameters 20% larger than those of the attached C atoms. These positions were updated every two cycles of refinement. All calculations were performed on a VAX station 3100.

The support of the Tulane University Department of Chemistry is gratefully acknowledged.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55792 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1036]

References

- Enraf-Nonius (1990). *MolEN*. An interactive structure solution procedure. Enraf-Nonius, Delft, The Netherlands.
- Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80*. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England, and Louvain, Belgium.
- Nohara, T., Kashiwada, Y., Murkami, K., Tomimatsu, T., Kido, M., Yagi, A. & Nishioka, I. (1981). *Chem. Pharm. Bull.* **29**, 2451–2459.
- Nohara, T., Kashiwada, Y., Tomimatsu, T., Kido, M., Tokubushi, N. & Nishioka, I. (1980). *Tetrahedron Lett.* **21**, 2647–2648.
- Schagen, J. D., Staver, L., van Meurs, F. & Williams, G. (1989). *CAD-4* Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Shea, K. J., Lease, T. G. & Ziller, J. W. (1990). *J. Am. Chem. Soc.* **112**, 8627–8629.
- Shea, K. J., Staab, A. J. & Zandi, J. S. (1991). *Tetrahedron Lett.* **32**, 2715–2718.
- Shea, K. J., Wise, S., Burke, L. D., Davis, P. D., Gilman, J. W. & Creeley, A. C. (1982). *J. Am. Chem. Soc.* **104**, 5708–5715.

Acta Cryst. (1993). **C49**, 998–1000

5,5-Bis(4-cyano-2-oxabutyl)-1,9-dicyano-3,7-dioxanonane

GEORGE R. NEWKOME,* CLAUS D. WEIS AND
XIAOFENG LIN

Center for Molecular Design and Recognition,
Department of Chemistry, University of South Florida,
Tampa, Florida 33620, USA

FRANK R. FRONCZEK

Department of Chemistry, Louisiana State University,
Baton Rouge, Louisiana 70803, USA

(Received 6 April 1992; accepted 23 November 1992)

Abstract

The pentaerythritol derivative, 5,5-bis(4-cyano-2-oxabutyl)-3,7-dioxanonane-1,9-dicarbonitrile, adopts a four-directional conformation in which each of the four appendages attached to the central C atom is extended with torsion angles within 30° of *anti*, except for that about the OC—CCN bond, which is *gauche*. One cyanomethyl group exhibits unresolved disorder.

Comment

The porosity of polyfunctionalized dendritic macromolecules is based, in part, on the microenvironment

instilled by the initial four-directional core (Newkome, Nayak, Behera, Moorefield & Baker, 1992; Newkome, Moorefield & Baker, 1992; Newkome & Lin, 1991; Newkome, Moorefield, Baker, Johnson & Behera, 1991). Treatment of pentaerythritol with acrylonitrile, using Burson's procedure (Burson, 1946), afforded one-step entry to the title compound (m.p. 312–313 K), which is an ideal polyfunctional core. In view of steric constraints in the carbon analogue, which has been reported (Newkome, Arai, Fronczek, Moorefield, Lin & Weis, 1993), the introduction of ethereal moieties in the inner lipophilic regions may circumvent part of these steric issues as well as instill new binding centers. Initial computational analysis of this compound indicated two nearly identical energetically equivalent conformers; thus a structural confirmation was deemed necessary prior to polymer construction.

This study confirms the four-directional conformation with extended chains, having *gauche*-oriented terminal cyano groups in the crystal structure. Torsion angles chemically equivalent to C1—C2—O1—C3 range 149.9 (2)–162.8 (2)° in magnitude, those equivalent to C2—O1—C3—C4 range 163.3 (6)–179.2 (2)° and those equivalent to O1—C3—C4—C5 range 35.5 (11)–57.7 (3)°, with the sign of O1—C3—C4—C5 being opposite to the other three. The value of the O4—C15—C16—C17 torsion angle, involving C16, as well as the values of the bond distances in that CH₂CN group, are uncertain as a result of the unresolved disorder. However, it is clear that the cyano groups alternate above and below the best plane of the remainder of the molecule.

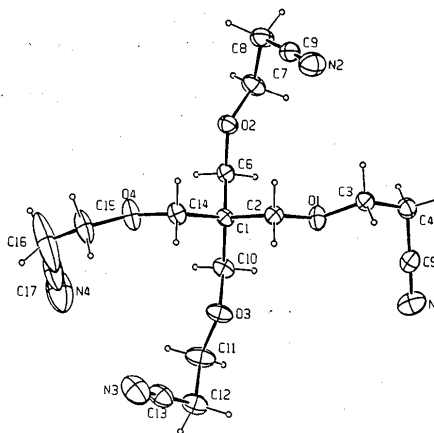


Fig. 1. The title molecule with thermal ellipsoids drawn at the 30% probability level and H atoms drawn as circles of arbitrary radii.

Experimental

Crystal data

C₁₇H₂₄N₄O₄
M_r = 348.4

Cu Kα radiation
λ = 1.54184 Å