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Dimethyl (\pm)-(1*S**,2*R**,3*S**)-[3-Phenyl-1-(*N*-phenylcarbamoyloxy)-2,3-epoxypropyl]phosphonate

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Abstract

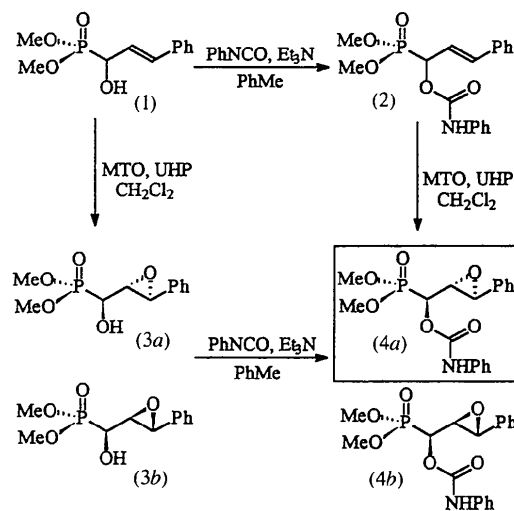
The crystal structure of the racemic title compound, C₁₈H₂₀NO₆P (m.p. 428–431 K), has been determined by X-ray diffraction. The title compound consists of a tetrahedral P atom bonded to two methoxy groups, and an alkyl chain. The alkyl chain is substituted at position 1 with a carbamate and with an epoxide at positions 2 and 3. The relative configuration of the 1-carbamate and 2,3-epoxide substituents was confirmed as *anti* (1*S*,2*R*,3*S*). The crystal structure contains an enantiomeric pair with two intermolecular hydrogen

bonds in a 14-membered ring. The hydrogen bonds are formed between the P=O of one enantiomer and the N—H of the other.

Comment

Methyl trioxorhenium (MTO) when combined with aqueous hydrogen peroxide forms peroxy adducts capable of the epoxidation of alkenes (Herrmann, Fischer & Marz, 1991; Herrmann, Fischer, Scherer & Wauch, 1993; Herrmann, Fischer, Rauch & Scherer, 1994; Al-Ajlouni & Espenson, 1995). However, one of the potential shortcomings of this reagent combination is the need for a protic solvent which may lead to the destruction of sensitive products (Herrmann, Fischer, Rauch & Scherer, 1994) or a reduction in the stereoselectivity due to competitive hydrogen bonding by the solvent (Murray, Singh, Williams & Moncrieff, 1995). Realizing the potential need for a non-protic variant of this reagent system, we initiated a study (Boehlow & Spilling, 1997) to examine urea hydrogen peroxide (UHP) (Heaney, 1993) as a reoxidant of MTO in non-protic solvents for the catalytic epoxidation of alkenes.

During this study, we oxidized the allylic hydroxyphosphonate (1) and its carbamate derivative (2) to give diastereoisomeric mixtures of epoxides (3) (3.5:1) and (4) (1:3.8), respectively. The epoxide diastereoisomers were correlated by converting the epoxyalcohol (3) into the epoxycarbamate (4) with phenyl isocyanate. Interestingly, the allylic hydroxyphosphonate (1) and the carbamate (2) showed a preference for the opposite epoxide diastereoisomers. However, the relative stereochemistry of the epoxide diastereoisomers remained unconfirmed.



In an earlier experiment, the carbamate (2) was oxidized with dimethyl dioxirane (DMD) to give the epoxide isomers (4) in a 1:1 ratio. The epoxide isomer (4a) [major isomer from (2) with MTO/UHP] was isolated

from this mixture by crystallization from diethyl ether as small needles (see *Experimental*). Slow diffusion of hexane into a dilute diethyl ether solution of the epoxy-carbamate at room temperature gave larger needles suitable for X-ray diffraction analysis. The crystal structure (Fig. 1) identified the epoxy-carbamate (*4a*) as the *anti* (1*S*,2*R*,3*S*) diastereoisomer. Therefore, the major isomer from oxidation of the allylic alcohol (*1*) was the *syn* diastereoisomer, since we had shown that it has the same relative stereochemistry as the minor epoxy carbamate isomer (*4b*). The solid-state structure contains an enantiomeric pair with two intermolecular hydrogen bonds in a 14-membered ring (Fig. 2). The hydrogen bonds are formed between the P=O of one enantiomer and the N—H of the other, with an intermolecular O4...H—N' distance of 2.889 (3) Å and a H—N' distance of 2.07 (3) Å.

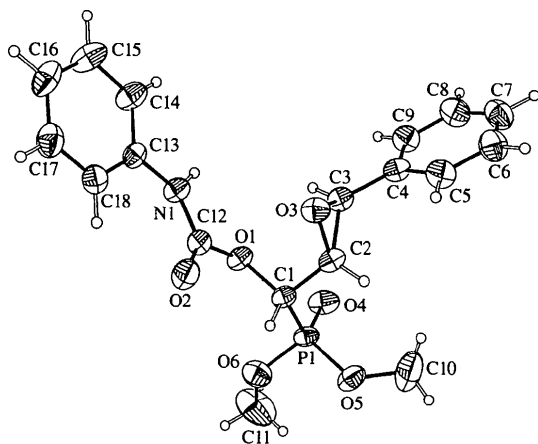


Fig. 1. The molecular structure of the racemic title compound, shown with 50% probability displacement ellipsoids.

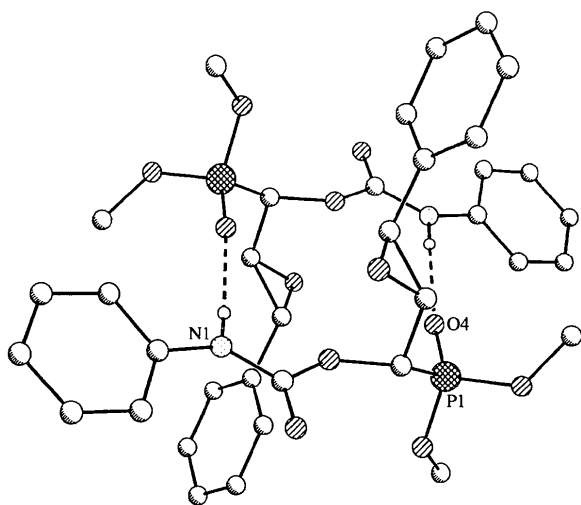


Fig. 2. The enantiomeric pair containing two intermolecular hydrogen bonds in a 14-membered ring (peripheral H atoms have been omitted for clarity).

Experimental

The title epoxide isomer (*4a*) was isolated by crystallization from diethyl ether as small needles. Slow diffusion of hexane into a dilute diethyl ether solution of the epoxy-carbamate at room temperature gave larger needles (m.p. 428–432 K) of suitable dimensions for X-ray diffraction analysis.

Crystal data

C₁₈H₂₀NO₆P

$M_r = 377.32$

Monoclinic

$P2_1/c$

$a = 11.8479 (1) \text{ \AA}$

$b = 9.4494 (2) \text{ \AA}$

$c = 17.8596 (3) \text{ \AA}$

$\beta = 108.384 (1)^\circ$

$V = 1897.44 (5) \text{ \AA}^3$

$Z = 4$

$D_x = 1.321 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 5216 reflections

$\theta = 2.0\text{--}22.0^\circ$

$\mu = 0.178 \text{ mm}^{-1}$

$T = 193 (2) \text{ K}$

Rectangular

$0.35 \times 0.15 \times 0.10 \text{ mm}$

Colorless

Data collection

Siemens CCD diffractometer

ω scans

Absorption correction: none

12 185 measured reflections

3924 independent reflections

2917 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.054$

$\theta_{\text{max}} = 26.50^\circ$

$h = -15 \rightarrow 12$

$k = -12 \rightarrow 12$

$l = -17 \rightarrow 23$

Intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.055$

$wR(F^2) = 0.129$

$S = 1.147$

3878 reflections

264 parameters

H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0311P)^2$

$+ 1.6558P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.325 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.274 \text{ e \AA}^{-3}$

Extinction correction:

SHELXL93

Extinction coefficient:

0.0019 (5)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

P1—O4	1.464 (2)	C2—C3	1.457 (4)
P1—O6	1.553 (2)	C3—C4	1.483 (4)
P1—O5	1.566 (2)	C4—C9	1.385 (4)
P1—C1	1.806 (2)	C4—C5	1.388 (4)
O1—C12	1.371 (3)	C5—C6	1.381 (4)
O1—C1	1.437 (3)	C6—C7	1.387 (4)
O2—C12	1.211 (3)	C7—C8	1.372 (4)
O3—C2	1.430 (3)	C8—C9	1.375 (4)
O3—C3	1.456 (3)	C13—C14	1.382 (4)
O5—C10	1.427 (4)	C13—C18	1.385 (4)
O6—C11	1.439 (4)	C14—C15	1.385 (4)
N1—C12	1.340 (3)	C15—C16	1.377 (4)
N1—C13	1.419 (3)	C16—C17	1.373 (4)
C1—C2	1.508 (4)	C17—C18	1.384 (4)
O4—P1—O6	116.40 (12)	C9—C4—C5	119.1 (3)
O4—P1—O5	114.61 (11)	C9—C4—C3	117.9 (2)
O6—P1—O5	104.34 (11)	C5—C4—C3	123.0 (2)
O4—P1—C1	115.19 (11)	C6—C5—C4	120.2 (3)
O6—P1—C1	101.23 (11)	C5—C6—C7	120.2 (3)
O5—P1—C1	103.26 (11)	C8—C7—C6	119.5 (3)
C12—O1—C1	114.8 (2)	C7—C8—C9	120.5 (3)

C2—O3—C3	60.7 (2)	C8—C9—C4	120.5 (3)
C10—O5—P1	123.3 (2)	O2—C12—N1	127.9 (2)
C11—O6—P1	121.1 (2)	O2—C12—O1	123.0 (2)
C12—N1—C13	125.4 (2)	N1—C12—O1	109.1 (2)
O1—C1—C2	109.4 (2)	C14—C13—C18	119.6 (3)
O1—C1—P1	108.0 (2)	C14—C13—N1	117.2 (2)
C2—C1—P1	110.9 (2)	C18—C13—N1	123.2 (2)
O3—C2—C3	60.5 (2)	C13—C14—C15	120.2 (3)
O3—C2—C1	115.4 (2)	C16—C15—C14	120.5 (3)
C3—C2—C1	121.1 (2)	C17—C16—C15	118.9 (3)
O3—C3—C2	58.80 (15)	C16—C17—C18	121.5 (3)
O3—C3—C4	118.1 (2)	C17—C18—C13	119.3 (3)
C2—C3—C4	124.1 (2)		

Intensity decay was monitored by recollecting the first 50 frames at the end of data collection (8.5 h). A total of 1325 frames (15 s frame⁻¹, 0.3° scan width) was collected. The structure was solved by direct methods and refined successfully in the monoclinic space group *P2₁/c*. Full-matrix least-squares refinement was carried out by minimizing $w(F_o^2 - F_c^2)^2$. The non-H atoms were refined anisotropically, whereas H atoms connected to C1, C2, C3 and N1 were refined isotropically to convergence. The rest of the H atoms were refined using an appropriate riding model. Very fine needles of 0.15 mm in the largest dimension were obtained initially from the diethyl ether solution and data collection was attempted on these crystals. To our surprise, the structure could be solved and partially refined using the CCD system. We are convinced that with the use of sensitive detectors such as the CCD area-detector system, single-crystal X-ray diffraction can truly be used as an analytical tool. Some pertinent data for the small crystal are presented here: $a = 11.9099$ (14), $b = 9.4878$ (11), $c = 17.946$ (2) Å, $\beta = 108.660$ (3)°, $V = 1921.2$ (4) Å³; 6367 reflections collected, 1793 independent reflections, $R1 = 0.103$, $wR2 = 0.260$, crystal dimensions = $0.15 \times <0.03 \times <0.03$ mm, data collection time 21 h (45 s frame⁻¹).

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1995). Software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: PT1044). Services for accessing these data are described at the back of the journal.

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The Khellin Quinone

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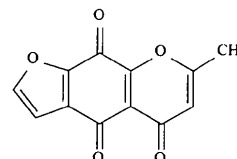
(Received 1 April 1997; accepted 14 July 1997)

Abstract

The title compound, 2-dehydro-2-methyl-5,8-dioxo-5,8-dihydrofuro[3,2-*g*]chromen-4-one, C₁₂H₆O₅, derives from the khellin molecule (7-methyl-4,9-dimethoxy-5H-furo[3,2-*g*][1]benzopyran-5-one). The molecular skeleton is nearly planar as in all furobenzopyranones. The intermolecular interactions are strengthened by C—H···O bonds.

Comment

The title compound, (I), has been studied in order to elucidate the transformation of khellin to khellinquinone.



(I)

The molecular skeleton is nearly planar (Fig. 1) as in all furobenzopyranones (El-Sayed, Ammon & Abd El-Rahman, 1988) and the crystal structure is made up of layers. The maximum deviation from the least-