Dimethyl (±)-(1S*,2R*,3S*)-[3-Phenyl-1-(N-Phenylcarbamoyloxy)-2, 3-Epoxypropyl]-Phosphonate

T. Boehlow
A. De La Cruz
N. Rath
University of Missouri–St. Louis
C. Spilling
University of Missouri–St. Louis

Follow this and additional works at: https://irl.umsl.edu/chemistry-faculty

Part of the Chemistry Commons

Recommended Citation
Boehlow, T.; De La Cruz, A.; Rath, N.; and Spilling, C., "Dimethyl (±)-(1S*,2R*,3S*)-[3-Phenyl-1-(N-Phenylcarbamoyloxy)-2, 3-Epoxypropyl]-Phosphonate" (1997). Chemistry & Biochemistry Faculty Works. 22.
DOI: https://doi.org/10.1107/S0108270197010408
Available at: https://irl.umsl.edu/chemistry-faculty/22

This Article is brought to you for free and open access by the Chemistry and Biochemistry at IRL @ UMSL. It has been accepted for inclusion in Chemistry & Biochemistry Faculty Works by an authorized administrator of IRL @ UMSL. For more information, please contact marvinh@umsl.edu.
Supplementary data for this paper are available from the IUCr electronic archives (Reference: MUI315). Services for accessing these data are described at the back of the journal.

References


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

TODD BOEHLLOW, ANTONETTE DE LA CRUZ, NIGAM P. RATH AND CHRISTOPHER D. SPILLING
Department of Chemistry, University of Missouri–St. Louis, 8001 Natural Bridge Road, St. Louis, MO 63121, USA.
E-mail: nigam.rath@umsl.edu
(Received 22 February 1996; accepted 22 July 1997)

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 (1S,2R,3S). 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 (Boehllow & 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 diastereomeric 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 epoxycarbamate at room temperature gave larger needles suitable for X-ray diffraction analysis. The crystal structure (Fig. 1) identified the epoxycarbamate (4a) as the *anti* (1S,2R,3S) 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.

**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 epoxycarbamate at room temperature gave larger needles (m.p. 428–432 K) of suitable dimensions for X-ray diffraction analysis.

**Crystal data**

C₁₈H₂₀NO₆P

$M_r = 377.32$

Mo Kα radiation

$\lambda = 0.71073$ Å

Cell parameters from 5216 reflections

$\theta = 2.0–22.0^\circ$

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

$T = 193$ (2) K

Rectangular

$0.35 \times 0.15 \times 0.10$ mm

Colorless

**Data collection**

Siemens CCD diffractometer

$\omega$ scans

Absorption correction: none

12,185 measured reflections

3924 independent reflections

2917 reflections with $I > 2\sigma(I)$

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

$w = 1/[\sigma^2(F^2) + (0.0311P)^2 + 1.6558P]$ where $P = (F^2 + 2F^2)/3$

$R_{	ext{max}} = 0.054$

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

$\Delta F_{\text{max}} = 0.325$ e Å$^{-3}$

$\Delta F_{\text{min}} = -0.274$ e Å$^{-3}$

Extinction correction: SHELXL93

Scattering factors from *International Tables for Crystallography* (Vol. C)

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

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Value</th>
<th>Bond/Angle</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1—O4</td>
<td>1.464 (2)</td>
<td>C2—C3</td>
<td>1.457 (4)</td>
</tr>
<tr>
<td>P1—O6</td>
<td>1.553 (2)</td>
<td>C3—C4</td>
<td>1.483 (4)</td>
</tr>
<tr>
<td>P1—O5</td>
<td>1.566 (2)</td>
<td>C4—C9</td>
<td>1.385 (4)</td>
</tr>
<tr>
<td>P1—C1</td>
<td>1.806 (2)</td>
<td>C4—C5</td>
<td>1.388 (4)</td>
</tr>
<tr>
<td>O1—C12</td>
<td>1.371 (3)</td>
<td>C5—C6</td>
<td>1.381 (4)</td>
</tr>
<tr>
<td>O1—C1</td>
<td>1.437 (3)</td>
<td>C6—C7</td>
<td>1.387 (4)</td>
</tr>
<tr>
<td>O2—C12</td>
<td>1.211 (3)</td>
<td>C7—C8</td>
<td>1.372 (4)</td>
</tr>
<tr>
<td>O3—C2</td>
<td>1.430 (3)</td>
<td>C8—C9</td>
<td>1.375 (4)</td>
</tr>
<tr>
<td>O3—C3</td>
<td>1.456 (3)</td>
<td>C9—C10</td>
<td>1.382 (4)</td>
</tr>
<tr>
<td>O5—C10</td>
<td>1.427 (4)</td>
<td>C10—C11</td>
<td>1.385 (4)</td>
</tr>
<tr>
<td>O6—C11</td>
<td>1.439 (4)</td>
<td>C11—C12</td>
<td>1.385 (4)</td>
</tr>
<tr>
<td>N1—C12</td>
<td>1.340 (3)</td>
<td>C12—C13</td>
<td>1.377 (4)</td>
</tr>
<tr>
<td>N1—C13</td>
<td>1.419 (3)</td>
<td>C13—C14</td>
<td>1.373 (4)</td>
</tr>
<tr>
<td>C1—C2</td>
<td>1.508 (4)</td>
<td>C14—C15</td>
<td>1.384 (4)</td>
</tr>
<tr>
<td>O4—P1</td>
<td>1.164 (12)</td>
<td>C15—C16</td>
<td>1.19 (3)</td>
</tr>
<tr>
<td>O4—P1—O6</td>
<td>1.146 (11)</td>
<td>C16—C17</td>
<td>1.179 (2)</td>
</tr>
<tr>
<td>O6—P1—O5</td>
<td>1.043 (11)</td>
<td>C17—C18</td>
<td>1.230 (2)</td>
</tr>
<tr>
<td>O6—P1—C1</td>
<td>1.159 (11)</td>
<td>C18—O4</td>
<td>1.202 (3)</td>
</tr>
<tr>
<td>O6—P1—C2</td>
<td>1.012 (11)</td>
<td>O4—P1</td>
<td>1.159 (11)</td>
</tr>
<tr>
<td>O5—P1—C1</td>
<td>1.036 (11)</td>
<td>O4—P1—O6</td>
<td>1.146 (11)</td>
</tr>
<tr>
<td>C12—O1—C1</td>
<td>1.148 (2)</td>
<td>O4—P1—O5</td>
<td>1.043 (11)</td>
</tr>
</tbody>
</table>

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).
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.

Abstract

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

Comment

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-

References


© 1997 International Union of Crystallography
Printed in Great Britain - all rights reserved