C(1)	1.0677 (4)	0.005 (2)	0.5999 (2)	7.5 (3)
C(2)	1.0170 (3)	0.070 (1)	0.6491 (2)	5.4 (2)
C(3)	0.8884 (2)	−0.0947 (7)	0.6911 (1)	4.1 (2)
C(4)	0.8218 (3)	−0.2745 (8)	0.6891 (2)	4.8 (2)
C(5)	0.7539 (2)	−0.2626 (7)	0.7245 (2)	4.3 (2)
C(6)	0.7506 (2)	−0.0718 (6)	0.7624 (1)	3.8 (1)
C(7)	0.8192 (3)	0.1040 (7)	0.7645 (2)	4.8 (2)
C(8)	0.8881 (2)	0.0943 (8)	0.7289 (2)	4.7 (2)
C(9)	0.6736 (2)	−0.0514 (7)	0.7988 (1)	4.1 (2)
C(10)	0.5162 (2)	0.1966 (9)	0.8233 (2)	4.4 (2)
C(11)	0.5537 (2)	0.2103 (7)	0.8869 (1)	3.8 (1)
C(12)	0.6149 (3)	−0.0064 (8)	0.9060 (2)	4.8 (2)
C(13)	0.4736 (3)	0.2245 (8)	0.9229 (2)	4.6 (2)
C(14)	0.4150 (3)	0.4529 (7)	0.9154 (2)	4.6 (2)
C(15)	0.3349 (3)	0.4554 (7)	0.9507 (2)	4.7 (2)
C(16)	0.2756 (3)	0.6803 (7)	0.9439 (2)	4.6 (2)
C(17)	0.1956 (3)	0.6782 (8)	0.9793 (2)	5.2 (2)
C(18)	0.1416 (4)	0.910 (1)	0.9767 (2)	6.2 (2)

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

S(1)···S(2)	3.006 (1)	S(1)—C(9)	1.809 (4)
S(1)—C(10)	1.805 (4)	S(2)—C(9)	1.806 (4)
S(2)—C(12)	1.811 (4)	O(1)—C(2)	1.433 (5)
O(1)—C(3)	1.371 (4)	C(1)—C(2)	1.499 (6)
C(3)—C(4)	1.379 (5)	C(3)—C(8)	1.365 (5)
C(4)—C(5)	1.376 (5)	C(5)—C(6)	1.380 (4)
C(6)—C(7)	1.384 (5)	C(6)—C(9)	1.505 (4)
C(7)—C(8)	1.392 (5)	C(10)—C(11)	1.516 (5)
C(11)—C(12)	1.515 (5)	C(11)—C(13)	1.534 (4)
C(13)—C(14)	1.512 (5)	C(14)—C(15)	1.522 (5)
C(15)—C(16)	1.502 (5)	C(16)—C(17)	1.523 (5)
C(17)—C(18)	1.491 (6)		
C(9)—S(1)—C(10)	101.1 (2)	C(9)—S(2)—C(12)	100.3 (2)
C(2)—O(1)—C(3)	118.6 (3)	O(1)—C(2)—C(1)	106.4 (4)
O(1)—C(3)—C(4)	115.7 (3)	O(1)—C(3)—C(8)	124.3 (3)
C(4)—C(3)—C(8)	120.0 (3)	C(3)—C(4)—C(5)	120.3 (4)
C(4)—C(5)—C(6)	121.2 (4)	C(5)—C(6)—C(7)	117.5 (3)
C(5)—C(6)—C(9)	121.3 (3)	C(7)—C(6)—C(9)	121.2 (3)
C(6)—C(7)—C(8)	121.9 (4)	C(3)—C(8)—C(7)	119.1 (4)
S(1)—C(9)—S(2)	112.5 (2)	S(1)—C(9)—C(6)	108.8 (2)
S(2)—C(9)—C(6)	110.3 (2)	S(1)—C(10)—C(11)	115.8 (2)
C(10)—C(11)—C(12)	111.5 (3)	C(10)—C(11)—C(13)	110.3 (3)
C(12)—C(11)—C(13)	109.7 (3)	S(2)—C(12)—C(11)	115.9 (3)
C(11)—C(13)—C(14)	115.9 (3)	C(13)—C(14)—C(15)	114.0 (3)
C(14)—C(15)—C(16)	114.9 (3)	C(15)—C(16)—C(17)	114.0 (3)
C(16)—C(17)—C(18)	114.1 (4)		

Azimuthal scans of several reflections revealed no need for an absorption correction; intensities were corrected for Lorentz–polarization effects.

The structure was solved by direct methods using *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Beurskens, 1984). The non-H atoms were refined with anisotropic displacement parameters. H atoms, located by difference Fourier synthesis, were refined with isotropic displacement parameters. All calculations were performed using the *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1985). *ORTEP*II (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978) were used to prepare Figs. 1 and 2.

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References

Beurskens, P. T. (1984). *DIRDIF. Direct Methods for Difference Structures – an Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors*. Technical Report 1984/1. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.

Haramoto, Y., Akazawa, K. & Kamogawa, H. (1984). *Bull. Chem. Soc. Jpn*, **57**, 3173–3176.

Haramoto, Y. & Kamogawa, H. (1983). *J. Chem. Soc. Chem. Commun.* pp. 75–76.

Haramoto, Y. & Kamogawa, H. (1985a). *Bull. Chem. Soc. Jpn*, **58**, 477–480.

Haramoto, Y. & Kamogawa, H. (1985b). *Mol. Cryst. Liq. Cryst.* **131**, 101–107.

Haramoto, Y., Nobe, A. & Kamogawa, H. (1984). *Bull. Chem. Soc. Jpn*, **57**, 1966–1969.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Miyake, M., Haramoto, Y. & Kamogawa, H. (1994). *Acta Cryst.* C50, 805–807.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. Univ. of Cambridge, England.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

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(2S,3R,4S)-4-(1,1-Dimethylethoxycarbonyl-amino)-2,3-epoxy-5-phenylpentanoic Acid Ethyl Ester

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Abstract

The X-ray analysis of the title compound [alternative name: ethyl 4-(*tert*-butoxycarboxamido)-2,3-epoxy-5-phenylpentanoate, $C_{18}H_{25}NO_5$, was performed in order to prove the structure of the synthetic product with respect to the existence of a *trans* epoxide and to determine the relative configurations of atoms C(2) (*S*) and C(3) (*R*) with respect to the known chirality of atom C(4) (*S*). There are no unusual structural features in the crystal although the torsion angles between the epoxide and the carboxamido groups are noteworthy.

Comment

The title compound, (I), belongs to the class of α,β-epoxy esters (glycidic esters). It was obtained as the main product from the oxidation of 4(S)-(1,1-dimethylethoxycarbonylamino)-5-phenyl-2(E)-pentenoic acid ethyl ester with m-chloroperbenzoic acid. The α,β-unsaturated ester derivative has been synthesized in a three-step procedure starting from L-phenylalaninol. The γ-amino-α,β-epoxy ester thus obtained is a versatile building block for the synthesis of 2-hetero-substituted statine derivatives.

(I)
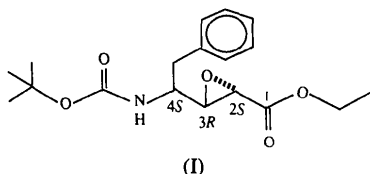
Chiral γ-N,N-dibenzylamino α,β-unsaturated esters can be epoxidized by tert-butylhydroperoxide and potassium tert-butoxide in a mixture of THF and ammonia (Reetz & Lauterbach, 1991a). This method is not suitable for the chiral γ-N-Boc-protected analogue, where Boc is tert-butoxycarbonyl. However, the highly diastereoselective epoxidation can be achieved using 3-chloroperbenzoic acid (MCPBA), yielding the title compound (Sandoz, 1993). Treatment of the above mentioned γ-N,N-dibenzylamino-protected derivatives with MCPBA does not result in epoxide formation. Instead, amine oxides are obtained which undergo subsequent [2,3]-sigmatropic rearrangement to hydroxylamines (Reetz & Lauterbach, 1991b).

Fig. 1 shows a stereoscopic view of the molecular conformation and the atomic numbering used. There is one weak intermolecular hydrogen bond between the carbonyl O atom O(41) and the amide N atom N(4) of length 3.08 Å [O(41)···H(4) 2.14 Å, N(4)—H···O(41)
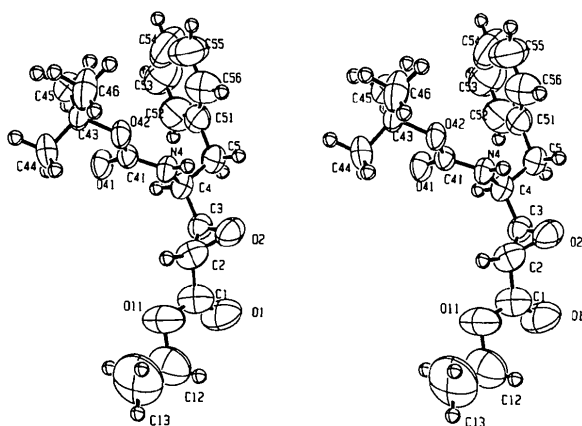
145°]. As can be seen from the ORTEP (Johnson, 1965) drawing of the title molecule, the atomic vibrational ellipsoids of the pentanoic acid and amide moieties are relatively small and isotropic, but large anisotropic displacement vibrations are observed for the terminal atoms of the phenyl, tert-butyl and ethyl groups. This is reflected in the slightly larger deviations of the structural parameters of these groups from standard values (see Table 2).

Experimental

Crystal data

$C_{18}H_{25}NO_5$	Cu $K\alpha$ radiation
$M_r = 335.40$	$\lambda = 1.5418$ Å
Monoclinic	Cell parameters from 25
C2	reflections
$a = 27.850\,(7)$ Å	$\theta = 35\text{--}45°$
$b = 5.217\,(3)$ Å	$\mu = 0.655$ mm^{-1}
$c = 13.463\,(4)$ Å	$T = 295$ K
$\beta = 80.57\,(2)°$	Needle
$V = 1929.7$ Å^3	$0.5 \times 0.2 \times 0.2$ mm
$Z = 4$	Colourless
$D_x = 1.15$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4F diffractometer	1752 observed reflections $[I > 3\sigma(I)]$
$\omega/2\theta$ scans	$R_{int} = 0.032$
Absorption correction:	$\theta_{max} = 72°$
ψ scan	$h = 0 \rightarrow 32$
(CADABS; Gould	$k = 0 \rightarrow 7$
& Smith, 1986)	$l = -16 \rightarrow 16$
$T_{min} = 0.99, T_{max} = 1.01$	3 standard reflections
1909 measured reflections	frequency: 60 min
1876 independent reflections	intensity decay: 2.1%

Refinement

Refinement on F	$w = 1/[\sigma^2(F) + 0.0007F^2]$
$R = 0.098$	$(\Delta/\sigma)_{max} = 0.32$
$wR = 0.109$	$\Delta\rho_{max} = 0.364$ e Å^{-3}
$S = 0.538$	$\Delta\rho_{min} = -0.276$ e Å^{-3}
1752 reflections	Atomic scattering fac-
217 parameters	tors from SHELX76
H-atom parameters not	(Sheldrick, 1976)
refined	

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

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

	x	y	z	U_{eq}
C(1)	0.1705 (3)	−0.1218 (23)	0.3979 (5)	0.106 (5)
O(1)	0.1604 (3)	−0.037 (3)	0.4805 (5)	0.145 (6)
C(2)	0.2175 (3)	−0.0884 (19)	0.3327 (4)	0.093 (4)
O(2)	0.24547 (20)	0.1334 (14)	0.3541 (5)	0.104 (3)
C(3)	0.26306 (20)	−0.1124 (4)	0.3740 (4)	0.073 (3)
C(4)	0.31081 (18)	−0.1898 (14)	0.3129 (3)	0.0682 (25)
N(4)	0.31181 (15)	−0.1550 (12)	0.2053 (3)	0.0634 (19)
C(5)	0.35166 (24)	−0.0337 (16)	0.3495 (4)	0.083 (3)
O(11)	0.14151 (21)	−0.2720 (23)	0.3561 (5)	0.141 (6)
C(12)	0.0903 (5)	−0.283 (4)	0.4176 (12)	0.173 (12)
C(13)	0.0669 (7)	−0.400 (7)	0.3549 (18)	0.29 (3)

Fig. 1. *ORTEP* (Johnson, 1965) stereoscopic view of the title molecule. Displacement ellipsoids of the non-H atoms are plotted at the 50% probability level with H atoms at a constant radius of 0.15 Å.

C(41)	0.32296 (16)	−0.3515 (13)	0.1396 (3)	0.0590 (21)
O(41)	0.32470 (17)	−0.5756 (11)	0.1651 (3)	0.0797 (22)
O(42)	0.33030 (14)	−0.2649 (11)	0.04534 (23)	0.0681 (18)
C(43)	0.34400 (20)	−0.444449 †	−0.0377 (3)	0.069 (3)
C(44)	0.3019 (3)	−0.6293 (14)	−0.0431 (5)	0.091 (3)
C(45)	0.3915 (3)	−0.5871 (19)	−0.0270 (6)	0.096 (4)
C(46)	0.3515 (4)	−0.2714 (16)	−0.1290 (5)	0.114 (4)
C(51)	0.40077 (22)	−0.1074 (17)	0.2957 (5)	0.089 (4)
C(52)	0.4240 (4)	−0.316 (3)	0.3300 (13)	0.146 (9)
C(53)	0.4696 (5)	−0.378 (4)	0.2742 (15)	0.171 (12)
C(54)	0.4904 (8)	−0.260 (5)	0.2029 (20)	0.242 (22)
C(55)	0.4647 (5)	−0.036 (5)	0.1630 (11)	0.171 (12)
C(56)	0.4220 (4)	0.029 (3)	0.2139 (9)	0.136 (8)

† The y coordinate of atom C(43) was fixed at the given value in order to fix the origin along y in space group C2.

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

C(1)—O(1)	1.185 (13)	C(5)—C(51)	1.489 (10)
C(1)—C(2)	1.462 (12)	O(11)—C(12)	1.529 (20)
C(1)—O(11)	1.316 (13)	C(12)—C(13)	1.30 (3)
C(2)—O(2)	1.450 (10)	C(41)—O(41)	1.222 (7)
C(2)—C(3)	1.472 (10)	C(41)—O(42)	1.331 (7)
O(2)—C(3)	1.415 (9)	O(42)—C(43)	1.461 (6)
C(3)—C(4)	1.500 (8)	C(43)—C(44)	1.530 (8)
C(4)—N(4)	1.455 (7)	C(43)—C(45)	1.545 (9)
C(4)—C(5)	1.544 (9)	C(43)—C(46)	1.512 (10)
N(4)—C(41)	1.356 (7)		
C(2)—C(1)—O(1)	124.9 (9)	C(51)—C(5)—C(4)	112.0 (6)
O(11)—C(1)—O(1)	123.5 (10)	C(12)—O(11)—C(1)	112.2 (10)
O(11)—C(1)—C(2)	111.5 (8)	C(13)—C(12)—O(11)	101.0 (17)
O(2)—C(2)—C(1)	115.7 (7)	O(41)—C(41)—N(4)	123.8 (5)
C(3)—C(2)—C(1)	120.3 (7)	O(42)—C(41)—N(4)	110.4 (5)
C(3)—C(2)—O(2)	57.9 (5)	O(42)—C(41)—O(41)	125.9 (5)
C(3)—O(2)—C(2)	61.8 (5)	C(43)—O(42)—C(41)	119.5 (4)
O(2)—C(3)—C(2)	60.3 (5)	C(44)—C(43)—O(42)	109.6 (4)
C(4)—C(3)—C(2)	123.8 (6)	C(45)—C(43)—O(42)	110.9 (4)
C(4)—C(3)—O(2)	116.3 (5)	C(45)—C(43)—C(44)	112.0 (5)
N(4)—C(4)—C(3)	112.5 (5)	C(46)—C(43)—O(42)	103.0 (5)
C(5)—C(4)—C(3)	108.4 (5)	C(46)—C(43)—C(44)	110.0 (5)
C(5)—C(4)—N(4)	110.9 (5)	C(46)—C(43)—C(45)	110.9 (5)
C(41)—N(4)—C(4)	121.3 (5)		

O(1)—C(1)—C(2)—O(2)	−24.0 (13)
O(1)—C(1)—C(2)—C(3)	42.2 (13)
O(11)—C(1)—C(2)—O(2)	160.1 (7)
O(11)—C(1)—C(2)—C(3)	−133.5 (8)
O(1)—C(1)—O(11)—C(12)	10.9 (15)
C(2)—C(1)—O(11)—C(12)	−173.2 (10)
C(1)—C(2)—O(2)—C(3)	111.1 (18)
C(1)—C(2)—C(3)—O(2)	−102.9 (8)
C(1)—C(2)—C(3)—C(4)	153.6 (7)
O(2)—C(2)—C(3)—C(4)	−103.3 (7)
C(2)—O(2)—C(3)—C(4)	115.6 (6)
C(2)—C(3)—C(4)—N(4)	19.5 (8)
C(2)—C(3)—C(4)—C(5)	142.6 (6)
O(2)—C(3)—C(4)—N(4)	−50.9 (7)
O(2)—C(3)—C(4)—C(5)	72.1 (7)
C(3)—C(4)—N(4)—C(41)	−124.7 (5)
C(5)—C(4)—N(4)—C(41)	113.6 (6)
C(3)—C(4)—C(5)—C(51)	177.4 (5)
N(4)—C(4)—C(5)—C(51)	−58.5 (7)
C(4)—N(4)—C(41)—O(41)	12.9 (8)
C(4)—N(4)—C(41)—O(42)	−168.5 (5)
C(4)—C(5)—C(51)—C(52)	−84.1 (10)
C(4)—C(5)—C(51)—C(56)	95.4 (10)
C(1)—O(11)—C(12)—C(13)	169.3 (15)
N(4)—C(41)—O(42)—C(43)	178.5 (4)
O(41)—C(41)—O(42)—C(43)	−3.0 (8)
C(41)—O(42)—C(43)—C(44)	66.1 (6)
C(41)—O(42)—C(43)—C(45)	−58.0 (6)
C(41)—O(42)—C(43)—C(46)	−176.8 (5)
C(5)—C(51)—C(52)—C(53)	178.6 (11)

Program used to solve the structure: *SHELX86* (Sheldrick, 1985). Program used for refinement: *SHELX76* (Sheldrick, 1976).

References

Gould, R. O. & Smith, D. E. (1986). *CADABS*. Univ. of Edinburgh, Scotland.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Reetz, M. T. & Lauterbach, E. H. (1991a). *Tetrahedron Lett.* **32**, 4477–4480.

Reetz, M. T. & Lauterbach, E. H. (1991b). *Tetrahedron Lett.* **32**, 4481–4482.

Sandoz (1993). European Patent Application 92/01 571.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELX86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.

Cyclic (1R,3R)-1,3-Dimethyltrimethylene [(5R)-2-Hydroxy-5-methyl-5-(2-methyl-1,3-dioxolan-2-yl)-1-cyclohexen-1-yl]-phosphonate, a Stable Enol

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Abstract

The title compound, $C_{16}H_{27}O_6P$, was obtained from the rearrangement of the corresponding vinyl phosphate. ^{31}P NMR experiments in solution have shown that this compound equilibrates to a mixture of three isomers in nearly equal proportions. In the crystalline state a single isomer is found which diffraction analysis identified as the enol form of the β-keto phosphonate having R stereochemistry at atom C(8).

Comment

The vinyl phosphate derivatives of some cyclic ketones are known to undergo rearrangement to the corresponding β-keto phosphonates upon treatment with strong base (Calogeropoulou, Hammond & Wiemer, 1987; An & Wiemer, 1992). When this reaction