There is extensive hydrogen bonding in the structure, with all potential donor and acceptor atoms participating.

The amino group interacts with three neighbouring molecules, O(4) of the carboxyl group and O(1) and O(2) of phosphonic acid groups. H(3) is donated to O(4) of a *c*-glide-related molecule, with N···O(4) and H(3)···O(4) distances and N—H(3)···O(4) angle of 2·869 (3), 1·99 (4) Å and 150 (3)°. H(4) is involved in a hydrogen bond with O(2) of a screw-related molecule. The N···O(2), H(4)···O(2) and N—H(4)···O(2) parameters in this case are 2·826 (3), 1·89 (4) Å and 172 (4)°. The third amino H atom, H(5), is donated to O(1) of the molecule one cell translation along **a**. The N—H(5)···O(1) [2·889 (3), 1·88 (4) Å and 163 (4)°] hydrogen bonds link molecules in a chain in the **a** direction.

The hydrogen-bonding scheme is completed with the formation of short hydrogen bonds from O(3) (phosphonic acid group) and O(5) (carboxyl group) to O(1) (related by a centre of symmetry) and O(2) (*c*-glide-related) of 2·595 (3) and 2·605 (3) Å. The H(1)···O(1) and H(2)···O(2) distances and O—H···O angles are 1·84 (4), 1·70 (4) Å and 169 (4), 171 (4)°, respectively.

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References

Ciunik, Z. & Głowiak, T. (1983). *Acta Cryst.* C**39**, 1271–1273.

Darriet, H., Darriet, J., Cassaigne, A. & Neuzil, E. (1975). *Acta Cryst.* B**31**, 469–471.

De Tinguy-Moreaud, E., Bioulac, B. & Neuzil, E. (1981). *Biochem. Soc. Trans.* **9**, 246–247.

Fukuyasu, H., Oya, Z., Kawakami, K., Kikuchi, T., Shomura, T., Tsuruoka, T., Watanabe, T., Kazuho, Y., Inouye, S. & Sekizawa, Y. (1978). German patent 2 823 346, 30 pp.; *Chem. Abstr.* (1979). **90**, P 133025s.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

IUPAC–IUB Commission on Biochemical Nomenclature (1970). *J. Mol. Biol.* **52**, 1–17.

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

Kondo, Y., Shomura, T., Ogawa, Y., Tsuruoka, T., Watanabe, H., Totzukawa, K., Suzuki, T., Moriyama, C., Yoshida, J., Inouye, S. & Niida, T. (1973). *Meiji Seika Kenkyu Nempo*, **13**, 34–42.

Kowalik, J., Kupczyk-Subotkowska, L. & Mastalerz, P. (1981). *Synthesis*, pp. 57–58.

Kowalik, J., Sawka-Dobrowolska, W., Głowiak, T. & Siatecki, Z. (1986). In the press.

Lehmann, M. S., Koetzle, T. F. & Hamilton, W. C. (1972). *J. Cryst. Mol. Struct.* **2**, 225–233.

Lehmann, M. S. & Nunes, A. C. (1980). *Acta Cryst.* B**36**, 1621–1625.

Lejczak, B., Starzemska, H. & Mastalerz, P. (1981). *Experientia*, **37**, 461–462.

Marsh, R. E. & Donohue, J. (1967). *Adv. Protein Chem.* **22**, 235–256.

Rupp, W., Finke, M., Beringer, H. & Lagenlueddeke, P. (1977). German patent No. 2 717 440, 22 pp.; *Chem. Abstr.* (1978). **88**, P 7049e.

Sawka-Dobrowolska, W. (1985). *Acta Cryst.* C**41**, 84–86.

Sawka-Dobrowolska, W., Głowiak, T., Siatecki, Z. & Soroka, M. (1985). *Acta Cryst.* C**41**, 453–456.

Sequeira, A., Rajagopal, H. & Chidambaram, R. (1972). *Acta Cryst.* B**28**, 2514–2519.

Syntex (1976). *XTL/XTLE Structure Determination System.* Syntex Analytical Instruments, Cupertino, California.

Acta Cryst. (1987). C**43**, 291–293

Structure of 2,5,5-Trimethyl-3-oxo-7-*t*-hydroxy-1-cycloheptanephosphonoacetic Acid γ-Lactone Diethyl Ester*

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Abstract. $C_{16}H_{27}O_6P$, $M_r = 346{\cdot}4$, triclinic, $P\bar{1}$, $a = 9{\cdot}812$ (5), $b = 9{\cdot}115$ (5), $c = 11{\cdot}857$ (4) Å, $\alpha = 116{\cdot}24$ (3), $\beta = 96{\cdot}45$ (4), $\gamma = 102{\cdot}57$ (4)°, $V = 901{\cdot}6$ (9) Å^3, $Z = 2$, $D_m = 1{\cdot}28$ (1), $D_x = 1{\cdot}276$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}18$ mm^{-1}, $F(000) = 372$, $T = 293$ K, $R = 0{\cdot}065$ for 1657 reflexions. The cycloheptane ring has a deformed boat conformation and is *cis*-fused with the γ-lactone at C(1)—C(7). The γ-lactone ring adopts an envelope

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* Diethyl (5,5,8-trimethyl-2,7-dioxoperhydro-3-oxazulen-1-yl)phosphonate.

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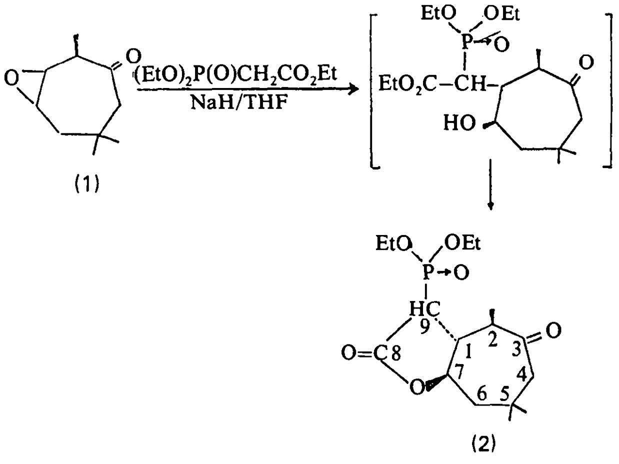
conformation with C(1) as the flap. The O(ethyl)—P—O—C torsion angles are 76·6 (7) and −108·9 (9)°. All bond lengths and angles are normal, apart from the ethyl groups which are affected by high thermal vibrations.

Introduction. In the search for lactones structurally related to biologically active natural lactones we have used 2,6,6-trimethyl-2,4-cycloheptadien-1-one derivatives as substrates in P—O olefination reactions. This reaction usually leads to the unsaturated esters, which are precursors for suitable lactones. Earlier studies (Bensel, Höhn, Marschall & Weyerstahl, 1979; Löcht, Marschall & Weyerstahl, 1982; Bensel, Marschall, Weyerstahl & Zeisberg, 1982) as well as our experiments (Orszańska & Rułko, 1982) show that under classic conditions of P—O olefination the phosphonic ylides attack carbonyl functions only.

However, when 3,4-epoxy-2,6,6-trimethylcycloheptanone (1) was used for such a reaction, we unexpectedly obtained a new lactone, with preservation of the carbonyl function. This unusual product may result from the nucleophilic opening of the epoxide ring followed by cyclization of the resulting hydroxy ester to the lactone. This process runs without destruction of the phosphonic ylide fragment as shown in the scheme.



The spectral data, *i.e.* IR, ^{1}H NMR, ^{13}C NMR and ^{31}P NMR (Orszańska & Rułko, 1984), allowed us to suggest the mechanism and the structure of the newly generated lactone compound (2). In this paper we report the X-ray results for compound (2).

Experimental. Clear colourless crystals grown from ether/*n*-hexane at room temperature, dimensions 0·4 × 0·5 × 0·3 mm; D_m by flotation in dichloromethane/1,2-dichloroethane; triclinic $P1$ or $P\bar{1}$ from Weissenberg photographs, $P\bar{1}$ was assumed; Syntex $P2_1$ computer-controlled four-circle diffractometer, scintillation counter, graphite monochromator; cell parameters by least squares from setting angles of 15 reflexions with $18 \leq 2\theta \leq 23°$ measured on diffractometer; 2508 independent reflexions; $2\theta_{max} = 46°$; variable θ–2θ scans, scan rate 2·0–29·3° min^{-1}, depending on intensity; two standards ($1\bar{1}\bar{4}$, 311) every 50 reflexions, variation in intensities ±3%; correction for Lorentz and polarization factors, not for absorption; 1657 with $I > 1{\cdot}96\sigma(I)$ used for structure determination; index range h 0 to 10, k −10 to 9, l −13 to 13; calculations performed with Syntex (1976) *XTL* system; neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); structure solved by direct methods, Syntex (1976) version of *MULTAN* (Germain, Main & Woolfson, 1971); full-matrix least squares, minimizing $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F)$; difference synthesis revealed nine H atoms, 12 H atoms placed at computer positions; H atoms of C_2H_5 groups could not be located; non-H atoms refined anisotropically, H atoms with fixed coordinates and isotropic $B = 5{\cdot}0$ Å^2; ethyl moieties vibrate strongly; $(\Delta/\sigma)_{max}$ in final LS cycle 0·05 for positional parameters and 0·11 for anisotropic temperature factors; max. and min. electron density in final difference map 0·38 and −0·37 e Å^{-3}; $R = 0{\cdot}065$, $wR = 0{\cdot}061$, $S = 3{\cdot}28$. Final positional parameters are given in Table 1.*

Table 1. *Positional parameters and equivalent isotropic temperature factors for the non-*H *atoms with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{1}{3}\textstyle\sum_{ii} B_{ii}.$$

	x	y	z	B_{eq}(Å^2)
P	0·1804 (2)	0·2778 (2)	0·0247 (2)	4·6 (2)
O(1)	0·2282 (6)	0·4321 (6)	−0·0021 (5)	8·4 (6)
O(2)	0·2934 (5)	0·1779 (6)	−0·0144 (4)	6·7 (5)
O(3)	0·0316 (5)	0·1757 (6)	−0·0310 (4)	5·4 (4)
O(4)	0·4736 (5)	0·5802 (5)	0·2589 (4)	5·9 (4)
O(5)	0·4406 (4)	0·3570 (5)	0·2968 (4)	4·8 (4)
O(6)	0·0571 (5)	0·2880 (6)	0·5420 (4)	6·0 (4)
C(1)	0·1852 (6)	0·2616 (7)	0·2547 (5)	3·0 (5)
C(2)	0·1274 (6)	0·3455 (7)	0·3768 (5)	3·6 (5)
C(21)	0·2184 (7)	0·5271 (7)	0·4803 (6)	4·4 (6)
C(3)	0·0880 (6)	0·2308 (7)	0·4393 (5)	3·7 (6)
C(4)	0·0881 (6)	0·0478 (7)	0·3666 (5)	3·8 (5)
C(5)	0·2429 (6)	0·0328 (7)	0·3888 (5)	3·8 (5)
C(51)	0·2442 (8)	−0·1412 (8)	0·2799 (7)	5·8 (7)
C(52)	0·2829 (7)	0·0379 (8)	0·5198 (6)	5·2 (6)
C(6)	0·3551 (6)	0·1825 (7)	0·3914 (5)	3·7 (5)
C(7)	0·3225 (6)	0·2124 (7)	0·2766 (5)	3·4 (5)
C(8)	0·3931 (7)	0·4555 (7)	0·2520 (5)	4·2 (6)
C(9)	0·2323 (6)	0·3827 (1)	0·1995 (5)	3·6 (5)
C(10)	0·2116 (16)	0·4330 (15)	−0·1179 (10)	15·4 (17)
C(11)	0·2411 (13)	0·5839 (12)	−0·1205 (9)	12·5 (13)
C(12)	0·2640 (11)	0·0089 (14)	−0·1291 (12)	11·5 (13)
C(13)	0·3740 (12)	−0·0206 (14)	−0·1772 (9)	12·2 (13)

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates, bond and torsion angles, and the results of least-squares-plane calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43350 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. Bond lengths are listed in Table 2. The molecular structure and the atom numbering are shown in Fig. 1 (*ORTEP*, Johnson, 1976).

The γ-lactone ring is slightly puckered. The average torsion-angle magnitude is 17·8°. The smallest torsion angle C(9)—C(8)—O(5)—C(7) is 1·4 (7)°, indicating near planarity for these four atoms, which deviate by a maximum of ±0·01 (1) Å from the mean plane through them. C(1) is −0·445 (5)° from this plane. The γ-lactone ring thus has an envelope conformation with C(1) as the flap [$\Delta C_s = 1\cdot7$ (8)°; Duax, Weeks & Rohrer (1976)], a conformation common among saturated γ-lactones (McPhail & Onan, 1976). The fusion to the cycloheptane ring is *cis* with torsion angles in the five- and seven-membered rings about the common bond of 27·0 (7) and 23·6 (7)°, respectively. Least-squares planes calculated through all combinations of four atoms show that in the cycloheptane ring C(2), C(3), C(5) and C(7) are coplanar to within ±0·002 (6) Å; C(1), C(4) and C(6) are displaced from the mean plane by 0·657 (5), 0·800 (6) and −0·802 (6) Å, respectively. O(6) is −0·606 (4) Å out of the plane. The cycloheptane ring thus adopts a deformed boat conformation with approximate C_s symmetry, the approximate mirror plane passing through C(6) and the midpoint of the C(2)—C(3) bond. The bond lengths and angles in the γ-lactone and cycloheptane moieties agree reasonably well with those found for other known structures (Weeks, Duax, Finnegan, Delecki & Kojić-Prodić, 1984; Rychlewska, 1985; and references cited therein).

Table 2. *Bond distances* (Å) *with e.s.d.'s in parentheses*

P—O(1)	1·562 (7)	C(7)—C(1)	1·540 (8)
P—O(2)	1·567 (6)	C(1)—C(9)	1·532 (9)
P—O(3)	1·443 (5)	C(1)—C(2)	1·548 (8)
P—C(9)	1·808 (6)	C(2)—C(21)	1·536 (9)
O(1)—C(10)	1·369 (13)	C(2)—C(3)	1·537 (9)
O(2)—C(12)	1·473 (14)	C(3)—O(6)	1·199 (7)
C(10)—C(11)	1·357 (18)	C(3)—C(4)	1·502 (9)
C(12)—C(13)	1·301 (16)	C(4)—C(5)	1·558 (9)
C(9)—C(8)	1·508 (9)	C(5)—C(51)	1·544 (10)
C(8)—O(4)	1·198 (9)	C(5)—C(52)	1·536 (9)
O(5)—C(8)	1·362 (8)	C(5)—C(6)	1·542 (9)
O(5)—C(7)	1·460 (8)	C(6)—C(7)	1·515 (8)

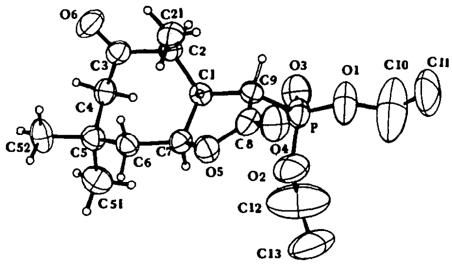

Fig. 1. The molecular structure of the title compound showing the atom labelling. Thermal ellipsoids are drawn at the 50% probability level.

The geometry around P is distorted tetrahedral, the angles varying from 115·8 (3) to 101·7 (3)°. All angles involving the non-ester O atom are greater than the others. The lengths of the esterified P—O bonds [1·562 (7) and 1·567 (6) Å] are close to those observed in the diethyl phosphates of magnesium, propylguanidinium, arginine and 2-amino-5,5-dimethyl-1-pyrrolinium (Ezra & Collin, 1973; Furberg & Solbakk, 1972, 1973; Griffith, Rutherford & Robertson, 1982). The length of the non-esterified P—O bond [1·443 (5) Å] compares well with similar bonds in the structures cited above. In the phosphonate ethyl groups the C—C bond lengths are unusually short and C—O—P and C—C—O angles are, respectively, greater than 120 and 110° and the thermal motion is very high. Similar effects have been reported for other diethyl phosphates (Hazel & Collin, 1972; Ezra & Collin, 1973).

The conformation of the diethyl phosphonate group is synclinal–anticlinal with the torsion angles C(10)—O(1)—P—O(2), ω, and C(12)—O(2)—P—O(1), ω^1, 76·6 (7) and −108·9 (8)°. The torsion angles P—O(1)—C(10)—C(11) and P—O(2)—C(12)—C(13) are 170·1 (13) and 151·6 (11)°, respectively.

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References

Bensel, N., Höhn, J., Marschall, H. & Weyerstahl, P. (1979). *Chem. Ber.* **112**, 2256–2277.

Bensel, N., Marschall, H., Weyerstahl, P. & Zeisberg, R. (1982). *Justus Liebigs Ann. Chem.* pp. 1781–1807.

Duax, W. L., Weeks, C. M & Rohrer, D. C. (1976). *Top. Stereochem.* **9**, 284–286.

Ezra, F. S. & Collin, R. L. (1973). *Acta Cryst.* B**29**, 1398–1403.

Furberg, S. & Solbakk, J. (1972). *Acta Chem. Scand.* **26**, 3699–3707.

Furberg, S. & Solbakk, J. (1973). *Acta Chem. Scand.* **27**, 1226–1232.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Griffith, E. A. H., Rutherford, J. S. & Robertson, B. E. (1982). *Acta Cryst.* B**38**, 2951–2955.

Hazel, J. P. & Collin, R. L. (1972). *Acta Cryst.* B**28**, 2951–2957.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

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

Löcht, G., Marschall, H. & Weyerstahl, P. (1982). *Justus Liebigs Ann. Chem.* pp. 1150–1157.

McPhail, A. T. & Onan, K. D. (1976). *J. Chem. Soc. Perkin Trans.* 2, pp. 332–335.

Orszańska, H. & Rułko, F. (1982). *Pol. J. Chem.* **56**, 1287–1296.

Orszańska, H. & Rułko, F. (1984). *Pol. J. Chem.* **58**, 697–703.

Rychlewska, U. (1985). *Acta Cryst.* C**41**, 540–542.

Syntex (1976). *XTL/XTLE Structure Determination System.* Syntex Analytical Instruments, Cupertino, California.

Weeks, C. M., Duax, W. L., Finnegan, R. A., Delecki, D. J. & Kojić-Prodić, B. (1984). *Acta Cryst.* C**40**, 1376–1378.