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**Stereochemistry of the Carroll  
Rearrangement: Structure of (+)-(2*R*)-2-  
[(1*R*,5*R*)-5-Methyl-2-oxocyclopentyl]-  
propionic Acid, C<sub>9</sub>H<sub>14</sub>O<sub>3</sub>**

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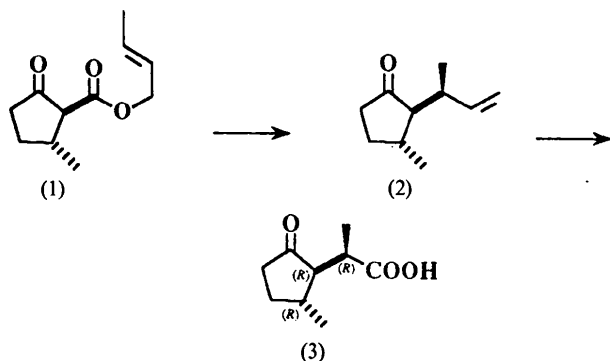
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**Abstract**

The configurations at the three chiral centres are *R*, *R* and *R*. The two substituents of the almost planar cyclopentanone are *trans* and the C2—C6—C10—C11 torsion angle is  $-79$  (1)°.

**Comment**

During studies on new stereoselective approaches to the Prelog–Djerassi lactone and related compounds (Ouvrard, Rodriguez & Santelli, 1993), we found that the Carroll rearrangement of the substituted optically active  $\beta$ -ketoester (1), obtained from (+)-(*R*)-pulegone, produced a good yield of the  $\gamma,\delta$ -ethylenic ketone (2) as a crucial precursor of  $\delta$ -lactones. Confirmation of the structure of (2) and determination of the stereochemistry of the rearrangement were achieved using the single-crystal X-ray analysis of the corresponding keto acid (3), easily obtained from (2) by oxidative cleavage of the double bond.



An intermolecular hydrogen bond exists between O12 and O4<sup>i</sup> [symmetry code: (i)  $x - 1, y, z$ ]: O12...H4—O4<sup>i</sup> = 2.738 Å.

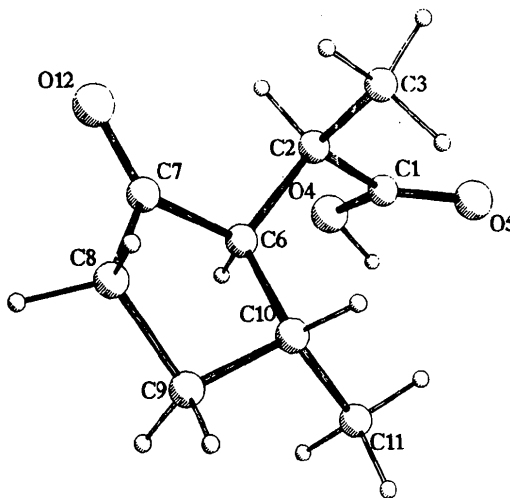


Fig. 1. View of the title compound showing the atom-numbering scheme.

**Experimental**

*Crystal data*

C<sub>9</sub>H<sub>14</sub>O<sub>3</sub>  
*M<sub>r</sub>* = 170.2  
Orthorhombic  
*P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>  
*a* = 7.335 (1) Å  
*b* = 9.277 (1) Å  
*c* = 13.211 (2) Å  
*V* = 898.9 (2) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.26 Mg m<sup>-3</sup>

Cu *K*α radiation  
 $\lambda$  = 1.5418 Å  
Cell parameters from 30 reflections  
 $\theta$  = 20.5–34.5°  
 $\mu$  = 0.78 mm<sup>-1</sup>  
*T* = 291 K  
Parallelepiped  
0.45 × 0.37 × 0.33 mm  
Colourless  
Crystal source: slow evaporation of CHCl<sub>3</sub>

*Data collection*

Huber four-circle and Rigaku rotating anode diffractometer  
 $\omega/2\theta$   
Absorption correction: none  
4504 measured reflections  
1613 independent reflections  
1597 observed reflections  
[*I* ≥ 2.5σ(*I*)]

*R*<sub>int</sub> = 0.04  
 $\theta_{\max}$  = 68°  
*h* =  $-8 \rightarrow 8$   
*k* =  $0 \rightarrow 11$   
*l* =  $0 \rightarrow 15$   
1 (138) standard reflection monitored every 50 reflections  
intensity variation: not significant

*Refinement*

Refinement on *F*  
*R* = 0.057  
*wR* = 0.066

( $\Delta/\sigma$ )<sub>max</sub> = 0.07  
 $\Delta\rho_{\max}$  = 0.30 e Å<sup>-3</sup>  
 $\Delta\rho_{\min}$  =  $-0.44$  e Å<sup>-3</sup>

S = 0.4  
1597 reflections  
174 parameters  
Only H-atom *U*'s refined  
 $w = 1/[\sigma^2(F) + 0.063F^2]$

Atomic scattering factors  
from *International Tables*  
for *X-ray Crystallography*  
(1974, Vol. IV)

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Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
C1	0.7928 (2)	0.0130 (2)	0.1325 (1)	0.035 (1)
C2	0.5853 (2)	0.0134 (2)	0.1381 (1)	0.034 (1)
C3	0.5157 (3)	-0.1262 (2)	0.1848 (1)	0.049 (1)
O4	0.8580 (2)	0.1457 (2)	0.1164 (1)	0.049 (1)
O5	0.8879 (2)	-0.0910 (2)	0.1418 (2)	0.055 (1)
C6	0.5031 (2)	0.0473 (2)	0.0325 (1)	0.033 (1)
C7	0.3007 (2)	0.0820 (2)	0.0400 (2)	0.035 (1)
C8	0.2028 (3)	0.0228 (3)	-0.0513 (2)	0.053 (1)
C9	0.3549 (3)	-0.0256 (2)	-0.1219 (2)	0.046 (1)
C10	0.5101 (3)	-0.0700 (2)	-0.0502 (1)	0.040 (1)
C11	0.6906 (3)	-0.0855 (3)	-0.1029 (2)	0.062 (1)
O12	0.2310 (2)	0.1514 (2)	0.1093 (1)	0.048 (1)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

C2—C1	1.524 (2)	O4—C1	1.338 (2)
O5—C1	1.197 (2)	C3—C2	1.523 (2)
C6—C2	1.552 (2)	C7—C6	1.523 (2)
C10—C6	1.543 (2)	C8—C7	1.507 (3)
O12—C7	1.230 (2)	C9—C8	1.522 (3)
C10—C9	1.537 (3)	C11—C10	1.503 (3)
O4—C1—C2	111.2 (2)	O5—C1—C2	125.4 (2)
O5—C1—O4	123.3 (1)	C3—C2—C1	110.6 (2)
C6—C2—C1	110.2 (1)	C6—C2—C3	114.0 (1)
C7—C6—C2	111.3 (2)	C10—C6—C2	118.8 (1)
C10—C6—C7	103.2 (1)	C8—C7—C6	109.6 (2)
O12—C7—C6	124.4 (2)	O12—C7—C8	126.0 (2)
C9—C8—C7	104.4 (1)	C10—C9—C8	104.1 (2)
C9—C10—C6	102.9 (1)	C11—C10—C6	115.1 (2)
C11—C10—C9	113.1 (2)		
O4—C1—C2—C3	-164	C10—C6—C7—O12	166
O4—C1—C2—C6	69	C2—C6—C10—C9	157
O5—C1—C2—C3	15	C2—C6—C10—C11	-79
O5—C1—C2—C6	-112	C7—C6—C10—C9	34
C1—C2—C6—C7	-167	C7—C6—C10—C11	157
C1—C2—C6—C10	73	C6—C7—C8—C9	-9
C3—C2—C6—C7	68	O12—C7—C8—C9	169
C3—C2—C6—C10	-52	C7—C8—C9—C10	30
C2—C6—C7—C8	-144	C8—C9—C10—C6	-40
C2—C6—C7—O12	38	C8—C9—C10—C11	-165
C10—C6—C7—C8	-15		

The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985). H atoms were placed in calculated positions, except for H(O4) which was found from difference Fourier maps. Anisotropic least-squares refinement was performed (*SHELX76*; Sheldrick, 1976); H atoms were treated isotropically with a common refined temperature factor ( $U = 0.06 \text{\AA}^2$ ).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71674 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1054]

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## 2,9-Dioxo-1,6,8,13-tetraoxadispiro[4.1.4.3]-tetradeca-3,10-diene, $\text{C}_{10}\text{H}_8\text{O}_6$

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## Abstract

The title tricyclic compound was obtained by photo-oxygenation of bis(5-formylfurfuryl) ether, followed by a dehydration reaction. The compound appears as a *trans* isomer, with respect to the relative positions of the lactonic rings to the dioxane ring, which remains chair shaped. Such a *trans* configuration has been found previously in anemonin, where the two lactonic rings are *trans* with respect to the cyclobutane ring.

## Comment

It is known that the photo-oxygenation of furfural derivatives may give hydroxybutenolides (Bernasconi *et al.*, 1984; Cottier, Descotes, Nigay, Parron &