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Product of a Paterno–Büchi Reaction of Pentafluorobenzaldehyde and 4-*tert*-Butyl-1-acetoxycyclohexene

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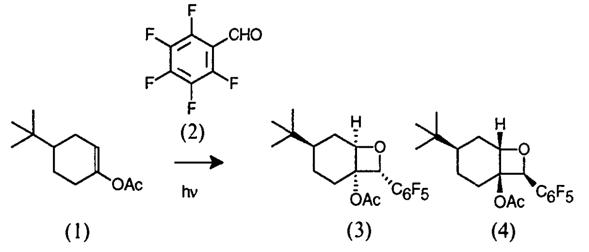
Abstract

The stereochemistry of the product of the photoaddition of pentafluorobenzaldehyde to 4-*tert*-butyl-1-acetoxycyclohexene, 4-*tert*-butyl-8-pentafluorophenyl-7-oxabicyclo[4.2.0]oct-1-yl acetate, $C_{19}H_{21}F_5O_3$, has been established. The ring fusion is *cis*, and the aryl and acetoxy substitutents are *trans* to the tertiary butyl group.

Comment

In the course of developing a synthesis for the 3-acetoxyoxetane subunit in the antineoplastic agent taxol (Wani, Taylor, Wall, Coggan & McPhail, 1971), we examined the prospects for using a Paterno–Büchi reaction (Paterno & Chietti, 1909; Büchi, Imman & Lipinsky, 1954) of enol acetates and benzaldehydes to introduce this particular moiety. The success of the methodology would depend upon the yields of the photoaddition reaction as well as of the subsequent oxidative degradation of the aromatic ring and a decarboxylation. Prior reports of the photoaddition reactions of enol ethers and trimethylsilyl enol ethers with aromatic aldehydes suggested that the regiochemistry desired in the taxol situation was favored (Jones, 1981). The photolysis of variously substituted benzaldehydes with enol acetates had not, however, been investigated (Vasudevan, Brock, Watt & Morita, 1994). The photolysis of 4-*tert*-butyl-1-acetoxycyclohexene (1) and pentafluorobenzaldehyde (2) gave preferentially a 2-aryl-3-acetoxyoxetane with the expected *cis* relationship between the pentafluorophenyl and acetoxy groups. It was difficult, however, to resolve the remaining stereochemical issue regarding the selectivity of the facial attack by (2): attack on the diastereotopic faces of (1) would lead either to the oxetane (3) or the oxetane (4). The structure determination confirmed that the product was, in fact, the oxetane (3).



In forming the oxetane (3) rather than (4), the pentafluorobenzaldehyde (2) underwent a preferential *syn* addition with respect to the *tert*-butyl group in the enol acetate (1). The factors which guide this unexpected diastereospecificity in this situation are unclear, but the steric influence of the *tert*-butyl group on attack by the triplet state of (2) would appear to be minimal. A kinetic preference for addition to the *re* face of the enol acetate (1) may reflect a transition state in which the acetyl group preferentially shields the *si* face. Molecular-mechanics calculations for 4-*tert*-butyl-1-acetoxycyclohexene (1) suggested that a conformation with the acetyl group twisted toward the *si* face (*i.e.* *syn* to the *tert*-butyl group) was more stable than other conformations with the acetyl in a quadrant above the *re* face. This same preference, if present in the transition state, would favor the formation of (3).

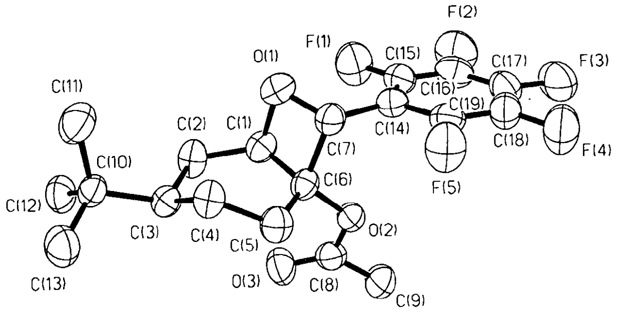


Fig. 1. Perspective drawing showing the molecular structure and the atom-numbering scheme. The shapes of the ellipsoids correspond to 50% probability contours of atomic displacement. The H atoms have been omitted for the sake of clarity.

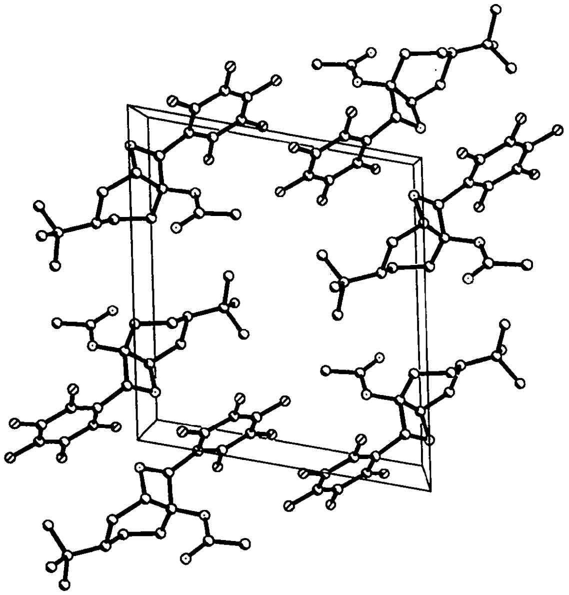


Fig. 2. Drawing of the unit cell. The *b* axis points from left to right, the *c* axis points upwards, and the *a* axis points out of the plane of the paper.

Experimental

The title compound was prepared as described by Vasudevan, Brock, Watt & Morita (1994).

Crystal data

$C_{19}H_{21}F_5O_3$
$M_r = 392.36$
Triclinic
$P\bar{1}$
$a = 6.2145$ (9) Å
$b = 11.5961$ (9) Å
$c = 12.8850$ (11) Å
$\alpha = 101.310$ (7)°
$\beta = 92.588$ (9)°
$\gamma = 91.661$ (8)°
$V = 908.9$ (2) Å^3
$Z = 2$
$D_x = 1.434$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 9.2$–$12.4°$
$\mu = 0.123$ mm^{-1}
$T = 295$ (2) K
Laths elongated along **a**; major faces are {001}, edge faces are {011}
0.3 × 0.3 × 0.1 mm
Colorless

Data collection

Enraf–Nonius CAD-4-VAX diffractometer
ω scans
Absorption correction: none
4154 measured reflections
4154 independent reflections
1157 observed reflections [$I > 2\sigma(I)$]

$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 8$
$k = -15 \rightarrow 15$
$l = -16 \rightarrow 16$
3 standard reflections frequency: 60 min intensity variation: <0.2%

Refinement

Refinement on F
$R = 0.047$
$wR = 0.040$
$S = 1.72$
1157 reflections
244 parameters
H-atom parameters not refined
Weighting scheme based on measured e.s.d.'s

$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.17$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

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

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

	x	y	z	$U_{\rm eq}$
F1	0.1270 (6)	0.8548 (3)	−0.0391 (3)	0.090 (2)
F2	0.1167 (6)	0.6506 (3)	−0.1732 (3)	0.097 (2)
F3	0.4398 (6)	0.5008 (3)	−0.1715 (2)	0.088 (2)
F4	0.7835 (6)	0.5618 (3)	−0.0313 (3)	0.091 (2)
F5	0.7937 (5)	0.7668 (3)	0.1060 (3)	0.080 (2)
O1	0.3398 (6)	1.0201 (3)	0.1125 (3)	0.063 (2)
O2	0.3110 (6)	0.7943 (3)	0.2242 (3)	0.047 (2)
O3	0.0571 (6)	0.8503 (3)	0.3393 (3)	0.066 (2)
C1	0.2024 (8)	0.9927 (4)	0.1940 (4)	0.047 (2)
C2	0.1436 (8)	1.1049 (4)	0.2705 (4)	0.053 (2)
C3	0.2898 (8)	1.1433 (4)	0.3708 (4)	0.042 (2)
C4	0.5182 (8)	1.0996 (4)	0.3515 (4)	0.048 (2)
C5	0.5133 (8)	0.9657 (4)	0.3273 (4)	0.051 (2)
C6	0.3759 (8)	0.9153 (4)	0.2285 (4)	0.042 (2)
C7	0.4824 (9)	0.9286 (5)	0.1262 (4)	0.050 (2)
C8	0.1453 (10)	0.7744 (5)	0.2833 (4)	0.050 (3)
C9	0.0926 (8)	0.6455 (4)	0.2677 (4)	0.063 (3)
C10	0.2813 (9)	1.2764 (4)	0.4200 (4)	0.045 (2)
C11	0.3850 (9)	1.3522 (4)	0.3496 (4)	0.069 (3)
C12	0.0476 (8)	1.3084 (4)	0.4349 (4)	0.061 (3)
C13	0.3998 (8)	1.3024 (4)	0.5288 (4)	0.067 (3)
C14	0.4641 (11)	0.8195 (5)	0.0383 (4)	0.045 (2)
C15	0.2972 (12)	0.7863 (6)	−0.0340 (5)	0.059 (3)
C16	0.2880 (11)	0.6798 (7)	−0.1047 (5)	0.063 (3)
C17	0.4503 (13)	0.6060 (6)	−0.1034 (5)	0.062 (3)
C18	0.6216 (11)	0.6350 (6)	−0.0345 (5)	0.059 (3)
C19	0.6244 (11)	0.7406 (5)	0.0355 (5)	0.054 (3)

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

F1—C15	1.348 (8)	C4—C5	1.522 (7)
F2—C16	1.343 (7)	C5—C6	1.508 (7)
F3—C17	1.354 (7)	C6—C7	1.534 (8)
F4—C18	1.340 (8)	C7—C14	1.521 (7)
F5—C19	1.346 (7)	C8—C9	1.492 (8)
O1—C1	1.460 (7)	C10—C11	1.530 (8)
O1—C7	1.434 (7)	C10—C12	1.521 (8)
O2—C6	1.438 (6)	C10—C13	1.526 (7)
O2—C8	1.349 (7)	C14—C15	1.356 (9)
O3—C8	1.188 (7)	C14—C19	1.368 (9)
C1—C2	1.534 (6)	C15—C16	1.382 (9)
C1—C6	1.528 (7)	C16—C17	1.344 (10)
C2—C3	1.530 (7)	C17—C18	1.346 (10)
C3—C4	1.535 (7)	C18—C19	1.371 (8)
C3—C10	1.553 (6)		
C1—O1—C7	91.6 (4)	C3—C10—C12	109.1 (4)
C6—O2—C8	116.7 (4)	C11—C10—C12	109.7 (4)
O1—C1—C2	111.3 (4)	C3—C10—C13	109.8 (4)
O1—C1—C6	89.9 (4)	C11—C10—C13	108.9 (4)
C2—C1—C6	119.5 (4)	C12—C10—C13	107.9 (4)
C1—C2—C3	116.8 (4)	C7—C14—C15	127.1 (6)
C2—C3—C4	110.3 (4)	C7—C14—C19	117.4 (5)
C2—C3—C10	113.5 (4)	C15—C14—C19	115.3 (5)
C4—C3—C10	114.3 (4)	F1—C15—C14	121.6 (5)
C3—C4—C5	110.0 (4)	F1—C15—C16	115.9 (6)
C4—C5—C6	111.9 (4)	C14—C15—C16	122.5 (6)
O2—C6—C1	115.8 (4)	F2—C16—C15	119.9 (6)
O2—C6—C5	111.9 (4)	F2—C16—C17	120.7 (6)
C1—C6—C5	117.4 (4)	C15—C16—C17	119.4 (6)
O2—C6—C7	110.3 (4)	F3—C17—C16	119.5 (6)
C1—C6—C7	85.3 (4)	F3—C17—C18	119.8 (6)
C5—C6—C7	113.3 (4)	C16—C17—C18	120.7 (6)

O1—C7—C6	90.7 (4)	F4—C18—C17	121.5 (5)
O1—C7—C14	115.1 (4)	F4—C18—C19	120.1 (6)
C6—C7—C14	114.9 (5)	C17—C18—C19	118.4 (6)
O2—C8—O3	123.6 (5)	F5—C19—C14	118.6 (5)
O2—C8—C9	110.3 (4)	F5—C19—C18	117.7 (6)
O3—C8—C9	126.1 (6)	C14—C19—C18	123.7 (6)
C3—C10—C11	111.4 (4)		

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *Software*. Data reduction: local program (Brock). Structure solution, structure refinement, molecular graphics and software used to prepare material for publication: *SHELXTL/PC* (Sheldrick, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1119). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two *N*-Saccharin Peracids

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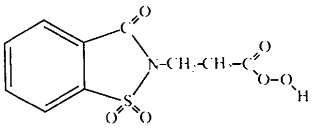
Abstract

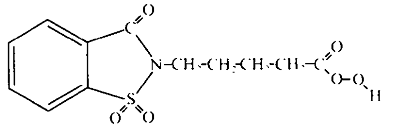
The crystal structures of *N*-saccharinperpropanoic acid [3-oxo-2*H*-1,2-benzisothiazole-2-peroxypropanoic acid 1,1-dioxide, $C_{10}H_9NO_6S$, (I)] and *N*-saccharinperpentanoic acid [3-oxo-2*H*-1,2-benzisothiazole-2-peroxypentanoic acid 1,1-dioxide, $C_{12}H_{13}NO_6S$, (II)] have been determined. Hydrogen bonding in (I) produces chains of molecules through the interaction of the peracid proton and keto O atom, while in (II) the result is ten-membered centrosymmetric peracid ring dimers. We believe this to be the first example of such a centrosymmetric motif in an organic peracid.

Comment

As part of a general study of the stability of organic peracids and peracid salts (Kariuki & Jones, 1990), and in particular of the role of hydrogen bonding in controlling the crystal structure of peracid and acid amides (Feeder & Jones, 1992), we report here the structures of *N*-saccharinperpropanoic acid, (I), and *N*-saccharinperpentanoic acid, (II).



(I)



(II)

In both compounds, the bond lengths and angles found for the saccharin moiety are similar to those reported for saccharin (Okaya, 1969), *N*-cyanomethylsaccharin (Junii, Guilan, Zhongyuan & Liu, 1989) and (*R*)-(+)-supidimide (Winter, Graudums & Frankus, 1983), and a series of saccharin derived carboxylic acids (Feeder & Jones, 1994*a*). The bond lengths and angles for the peracid function are not significantly different to those found for peroxypelargonic acid (Belitskus & Jeffrey, 1965), *o*-nitroperoxybenzoic acid (Sax, Beurskens & Chu, 1965) and *p*-nitroperoxybenzoic acid (Kim, Chu & Jeffrey, 1970), and for a series of *p*-amidoperbenzoic acids (Feeder & Jones, 1994*b*). The two sulfone O atoms in both structures lie approximately 1.2 Å out of the plane of the saccharin group.

The structure solution of (I) demonstrated that, except for the sulfone O atoms and the two methylene groups, the molecule is planar and lies on a crystallographic mirror plane. The two methylene groups are disordered across this mirror plane and the two C atoms were therefore refined with half occupancies. The methylene H atoms could not be located. The peroxycarboxylic acid proton was located in a reasonable position from the difference Fourier map, although it was found to refine with a very high isotropic displacement parameter. Hydrogen bonding within the structure of (I) generates

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