Crystal structure of (2*S*,4*S*,5*S*)-3-chlorobenzoic acid 2-*tert*-butyl-5-hydroxy-5-methyl-1,3-dioxan-4-yl ester, $C_{16}H_{21}ClO_5$

C. Wattenbach, H. Sippel, U. Müller and H. Frauenrath*

Universität Gh Kassel, Fachbereich 19 - Biologie/Chemie, Heinrich-Plett-Str. 40, D-34109 Kassel, Germany

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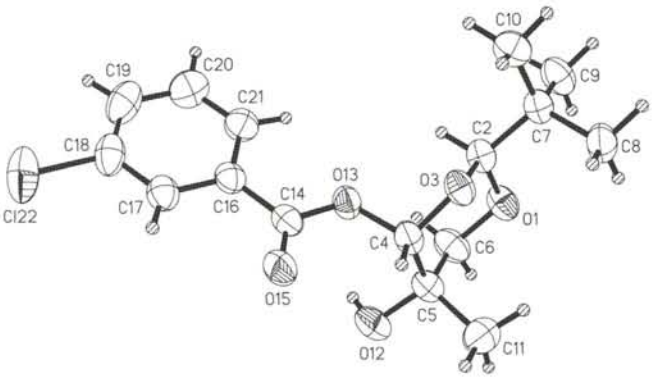

Abstract

$C_{16}H_{21}ClO_5$, monoclinic, $P12_11$ (No. 4), a = 5.986(1) Å, b = 24.551(1) Å, c = 11.574(1) Å, β = 100.50(1)°, V = 1672.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.027, $wR_{ref}(F^2)$ = 0.069, T = 297 K.

Source of material

To a stirred solution of (–)-2-*tert*-butyl-5-methyl-4*H*-1,3-dioxin (7.86 g, 50.3 mmol, $[\alpha]_D^{20}$ = –91.1 (neat), 92% ee) in 50 ml of THF commercial *m*-chloroperbenzoic acid was slowly added (14.88 g, 60.4 mmol, 70 % in water). After complete addition the solution was stirred for 4 h at room temperature. Then the solvent was removed under reduced pressure. The crude product was recrystallized from petroleum ether to give colourless needles (13.91 g, 84 %), mp 371 K, $[\alpha]_D^{20}$ = –110.1 (c=5, $CHCl_3$), 92 % ee.

Discussion

The crystal structure was determined to establish the relative configuration of the title compound. The title compound was rearranged in the presence of catalytic amounts of an acid to give a diastereomeric mixture of 2-*tert*-butyl-4-methyl-1,3-dioxolane-4-carboxaldehydes [1].

Table 1. Data collection and handling.

Crystal:	colourless needle, size 0.22 × 0.58 × 0.75 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.48 cm^{-1}
Diffractometer, scan mode:	Enraf Nonius CAD4, ω
$2\theta_{max}$:	49.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3153, 3009
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2664
$N(param)_{refined}$:	561
Programs:	SHELX-97 [2], ZORTEP [3]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	2*a*	0.343(4)	0.238(1)	0.028(2)	0.033(6)
H(2)	2*a*	0.921(4)	0.264(1)	0.131(2)	0.030(6)
H(3A)	2*a*	0.344(5)	0.293(1)	0.183(3)	0.041(7)
H(3B)	2*a*	0.402(5)	0.267(2)	0.321(3)	0.060(9)
H(4A)	2*a*	0.457(6)	0.071(2)	0.071(3)	0.059(9)
H(4B)	2*a*	0.489(6)	0.109(2)	0.186(4)	0.06(1)
H(4C)	2*a*	0.669(6)	0.112(1)	0.105(3)	0.056(9)
H(5A)	2*a*	0.087(6)	0.145(2)	0.112(4)	0.07(1)
H(5B)	2*a*	0.057(6)	0.108(2)	0.000(3)	0.07(1)
H(5C)	2*a*	0.011(7)	0.170(2)	–0.008(4)	0.07(1)
H(6A)	2*a*	0.561(6)	0.150(1)	–0.099(3)	0.053(9)
H(6B)	2*a*	0.320(7)	0.178(2)	–0.151(4)	0.08(1)
H(6C)	2*a*	0.352(6)	0.116(2)	–0.128(3)	0.07(1)
H(7A)	2*a*	0.805(7)	0.253(2)	0.415(4)	0.09(1)
H(7B)	2*a*	0.991(7)	0.251(2)	0.343(3)	0.08(1)
H(7C)	2*a*	0.808(6)	0.203(2)	0.313(3)	0.06(1)
H(8)	2*a*	0.630(7)	0.351(2)	0.243(4)	0.08(1)
H(9)	2*a*	0.975(6)	0.428(2)	–0.081(3)	0.055(9)
H(10)	2*a*	0.454(6)	0.484(2)	–0.303(3)	0.06(1)
H(11)	2*a*	0.219(7)	0.414(2)	–0.258(4)	0.09(1)
H(12)	2*a*	0.380(5)	0.352(1)	–0.101(3)	0.050(8)
H′(1)	2*a*	0.147(4)	0.492(1)	0.438(2)	0.032(6)
H′(2)	2*a*	0.636(4)	0.472(1)	0.322(2)	0.028(6)
H′(3A)	2*a*	0.045(5)	0.433(1)	0.280(2)	0.036(7)
H′(3B)	2*a*	–0.031(5)	0.454(1)	0.151(3)	0.051(8)
H′(4A)	2*a*	–0.162(7)	0.557(2)	0.479(4)	0.08(1)
H′(4B)	2*a*	–0.199(6)	0.585(1)	0.358(4)	0.06(1)
H′(4C)	2*a*	–0.142(9)	0.621(3)	0.469(5)	0.13(2)
H′(5A)	2*a*	0.261(7)	0.621(2)	0.584(4)	0.09(1)
H′(5B)	2*a*	0.212(7)	0.561(2)	0.606(4)	0.08(1)
H′(5C)	2*a*	0.447(6)	0.580(1)	0.556(3)	0.056(9)
H′(6A)	2*a*	0.379(7)	0.621(2)	0.346(3)	0.08(1)
H′(6B)	2*a*	0.137(7)	0.621(2)	0.272(4)	0.07(1)
H′(6C)	2*a*	0.179(8)	0.657(2)	0.377(4)	0.11(2)
H′(7A)	2*a*	0.555(7)	0.495(2)	0.117(4)	0.08(1)
H′(7B)	2*a*	0.300(8)	0.496(2)	0.048(5)	0.10(2)

* Correspondence author (e-mail: frauenra@hrz.uni-kassel.de)

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H'(7C)	2a	0.348(8)	0.533(2)	0.141(4)	0.11(2)
H'(8)	2a	0.3067	0.3976	0.1103	0.084
H'(9)	2a	0.250(5)	0.348(1)	0.471(3)	0.051(8)
H'(10)	2a	0.188(6)	0.268(2)	0.573(3)	0.07(1)
H'(11)	2a	0.497(6)	0.234(2)	0.715(3)	0.06(1)
H'(12)	2a	0.892(6)	0.355(1)	0.640(3)	0.056(9)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(22)	2a	0.8986(2)	0.51445(4)	–0.2352(1)	0.1008(7)	0.0481(4)	0.0995(7)	0.0028(4)	0.0473(6)	0.0213(5)
O(1)	2a	0.3850(3)	0.21321(8)	0.1939(2)	0.048(1)	0.043(1)	0.054(1)	–0.0095(8)	0.0233(9)	–0.0084(9)
C(2)	2a	0.4281(4)	0.2085(1)	0.0796(2)	0.035(1)	0.036(1)	0.047(2)	–0.000(1)	0.014(1)	–0.001(1)
O(3)	2a	0.6647(3)	0.21673(7)	0.0783(2)	0.0359(9)	0.0337(9)	0.053(1)	–0.0025(7)	0.0150(8)	–0.0033(8)
C(4)	2a	0.7531(4)	0.2661(1)	0.1251(2)	0.034(1)	0.032(1)	0.053(2)	–0.001(1)	0.007(1)	0.001(1)
C(5)	2a	0.6924(5)	0.2779(1)	0.2457(2)	0.043(2)	0.039(1)	0.050(2)	–0.003(1)	0.007(1)	–0.007(1)
C(6)	2a	0.4403(5)	0.2668(1)	0.2394(3)	0.051(2)	0.049(2)	0.059(2)	–0.006(1)	0.019(1)	–0.018(2)
C(7)	2a	0.3654(4)	0.1517(1)	0.0317(2)	0.038(1)	0.035(1)	0.049(2)	0.000(1)	0.010(1)	0.001(1)
C(8)	2a	0.5069(6)	0.1083(1)	0.1069(3)	0.052(2)	0.037(2)	0.063(2)	0.000(1)	0.008(1)	0.006(1)
C(9)	2a	0.1132(5)	0.1426(2)	0.0326(4)	0.043(2)	0.049(2)	0.077(2)	–0.007(1)	0.009(2)	–0.007(2)
C(10)	2a	0.4062(6)	0.1489(2)	–0.0943(3)	0.060(2)	0.051(2)	0.053(2)	–0.001(2)	0.010(2)	–0.008(2)
C(11)	2a	0.8368(7)	0.2420(2)	0.3364(3)	0.063(2)	0.067(2)	0.055(2)	–0.003(2)	0.003(2)	0.008(2)
O(12)	2a	0.7430(4)	0.33278(9)	0.2786(2)	0.058(1)	0.045(1)	0.064(1)	–0.009(1)	0.007(1)	–0.016(1)
O(13)	2a	0.6605(3)	0.30894(7)	0.0434(2)	0.0374(9)	0.0361(9)	0.050(1)	–0.0044(8)	0.0071(8)	0.0050(8)
C(14)	2a	0.8053(4)	0.3455(1)	0.0133(2)	0.042(1)	0.037(1)	0.043(1)	–0.007(1)	0.009(1)	–0.007(1)
O(15)	2a	1.0055(3)	0.34634(9)	0.0539(2)	0.042(1)	0.050(1)	0.063(1)	–0.0141(9)	–0.0016(9)	0.007(1)
C(16)	2a	0.6934(4)	0.3847(1)	–0.0760(2)	0.047(2)	0.035(1)	0.039(1)	–0.002(1)	0.012(1)	–0.006(1)
C(17)	2a	0.8249(5)	0.4259(1)	–0.1097(3)	0.051(2)	0.039(1)	0.048(2)	–0.002(1)	0.015(1)	–0.002(1)
C(18)	2a	0.7313(6)	0.4626(1)	–0.1945(3)	0.070(2)	0.039(2)	0.057(2)	0.004(1)	0.030(2)	0.003(1)
C(19)	2a	0.5065(6)	0.4584(2)	–0.2474(3)	0.079(2)	0.053(2)	0.059(2)	0.025(2)	0.021(2)	0.014(2)
C(20)	2a	0.3757(6)	0.4170(1)	–0.2143(3)	0.055(2)	0.065(2)	0.062(2)	0.013(2)	0.008(2)	0.002(2)
C(21)	2a	0.4655(5)	0.3803(1)	–0.1287(3)	0.046(2)	0.048(2)	0.049(2)	0.000(1)	0.008(1)	–0.003(1)
Cl'(2)	2a	0.9361(2)	0.26388(4)	0.79558(8)	0.0844(6)	0.0708(5)	0.0570(5)	0.0231(5)	0.0028(4)	0.0154(4)
O'(1)	2a	0.0439(3)	0.51392(8)	0.2730(2)	0.0365(9)	0.044(1)	0.051(1)	0.0036(8)	–0.0010(8)	–0.0057(9)
C'(2)	2a	0.1803(4)	0.5220(1)	0.3834(2)	0.034(1)	0.036(1)	0.045(1)	–0.003(1)	0.007(1)	0.000(1)
O'(3)	2a	0.4160(3)	0.51728(7)	0.3775(2)	0.0333(8)	0.0328(8)	0.051(1)	–0.0021(7)	0.0036(7)	–0.0040(8)
C'(4)	2a	0.4780(5)	0.4689(1)	0.3288(3)	0.036(1)	0.030(1)	0.051(2)	–0.002(1)	0.010(1)	0.001(1)
C'(5)	2a	0.3288(4)	0.4581(1)	0.2096(3)	0.043(1)	0.034(1)	0.049(2)	–0.003(1)	0.008(1)	–0.004(1)
C'(6)	2a	0.0825(5)	0.4614(1)	0.2262(3)	0.039(2)	0.040(2)	0.058(2)	–0.005(1)	0.000(1)	–0.010(1)
C'(7)	2a	0.1424(5)	0.5792(1)	0.4284(3)	0.041(1)	0.036(1)	0.051(2)	0.002(1)	0.008(1)	–0.002(1)
C'(8)	2a	–0.1097(6)	0.5852(2)	0.4346(4)	0.050(2)	0.058(2)	0.080(3)	0.008(2)	0.017(2)	–0.005(2)
C'(9)	2a	0.2840(7)	0.5854(2)	0.5511(3)	0.068(2)	0.056(2)	0.056(2)	0.009(2)	0.001(2)	–0.013(2)
C'(10)	2a	0.2112(7)	0.6220(1)	0.3463(4)	0.067(2)	0.039(2)	0.074(2)	0.001(2)	0.014(2)	0.010(2)
C'(11)	2a	0.3834(7)	0.4990(2)	0.1210(3)	0.067(2)	0.055(2)	0.048(2)	–0.002(2)	0.013(2)	0.003(2)
O'(12)	2a	0.3822(4)	0.40452(8)	0.1751(2)	0.055(1)	0.044(1)	0.068(1)	0.0021(9)	0.006(1)	–0.016(1)
O'(13)	2a	0.4520(3)	0.42343(7)	0.4042(2)	0.0363(9)	0.0377(9)	0.055(1)	–0.0012(7)	0.0053(8)	0.0076(8)
C'(14)	2a	0.6343(4)	0.4070(1)	0.4807(2)	0.041(2)	0.038(1)	0.043(2)	–0.001(1)	0.006(1)	–0.004(1)
O'(15)	2a	0.8157(4)	0.4290(1)	0.4956(2)	0.050(1)	0.062(1)	0.072(2)	–0.015(1)	–0.007(1)	0.017(1)
C'(16)	2a	0.5839(5)	0.3570(1)	0.5453(2)	0.047(1)	0.038(1)	0.038(1)	0.000(1)	0.010(1)	–0.005(1)
C'(17)	2a	0.3710(5)	0.3322(1)	0.5247(3)	0.050(2)	0.046(2)	0.043(2)	0.000(1)	0.008(1)	0.001(1)
C'(18)	2a	0.3374(6)	0.2859(1)	0.5868(3)	0.058(2)	0.055(2)	0.057(2)	–0.009(2)	0.018(2)	0.004(2)
C'(19)	2a	0.5112(6)	0.2641(2)	0.6693(3)	0.075(2)	0.048(2)	0.054(2)	0.004(2)	0.023(2)	0.010(2)
C'(20)	2a	0.7175(5)	0.2897(1)	0.6893(2)	0.063(2)	0.048(2)	0.039(2)	0.013(1)	0.012(1)	0.000(1)
C'(21)	2a	0.7582(5)	0.3359(1)	0.6282(2)	0.050(2)	0.039(1)	0.045(2)	0.002(1)	0.010(1)	–0.004(1)

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