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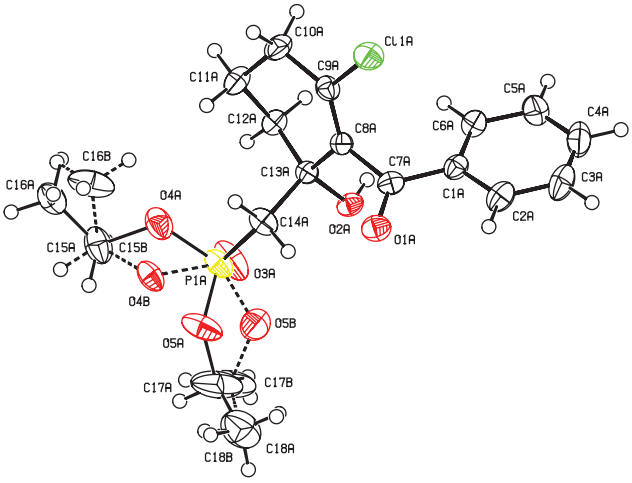
Crystal structure of 1-(diethoxy phosphonomethyl) 2-benzoyl-3-chloro-2-cyclohexen-1-ol, $C_{18}H_{24}ClO_5P$



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Abstract

$C_{18}H_{24}ClO_5P$, triclinic, $P\bar{1}$ (no. 2), $a = 11.5140(14)$ Å, $b = 11.5358(15)$ Å, $c = 15.582(2)$ Å, $\alpha = 76.106(2)°$, $\beta = 77.556(2)°$, $\gamma = 74.783(3)°$, $V = 1912.8(4)$Å^3, $Z = 4$, $R_{gt}(F) = 0.0481$, $wR_{ref}(F^2) = 0.1313$, $T = 173(2)$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Colorless prism
Size:	0.40 × 0.30 × 0.15 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	3.1 cm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω
$2\theta_{max}$, completeness:	50°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	10499, 6692, 0.026
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5210
$N(param)_{refined}$:	497
Programs:	Bruker programs [1, 3], SADABS [2], Platon [4]

Source of material

To a stirred solution of *n*-butyl lithium (1.6 M solution in hexane; 5.4 mL, 8.7 mmol) in THF (30 mL) at −65 °C was added dropwise with stirring a solution of diethyl methylphosphonate (1.22 g, 8.0 mmol) in THF (1 mL). The mixture was stirred at −65 °C for 30 min, and a solution of 2-benzoyl-3-chlorocyclohex-2-enone (1.89 g, 8.0 mmol) in THF (5 mL) was added. After 15 min at −65 °C, the mixture was allowed to warm up to room temperature and was then stirred for 1 h at this temperature. The mixture was quenched with saturated aqueous ammonium chloride and extracted with chloroform (3 × 30 mL). The chloroform extract was washed with water (2 × 20 mL), dried ($MgSO_4$), and filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography to afford the title compound as a colorless solid (1.71 g, 55%), 88–90 °C (1:3 EtOAc-Pet. ether, v/v). **Infrared spectrum**: υ_{max}: (ATR) 1265 (P = O), 1580 (C = C), 1658 (C = O) and 3267 (OH); **^{1}H-NMR** (300 MHz, $CDCl_3$) 1.29 (3H, t, *J* 7.2 Hz, 1 × CH_3 of POEt), 1.31 (3H, t, *J* 7.2 Hz, 1 × CH_3 of POEt), 1.78 (1H, m, 1 × H of CH_2), 2.01–2.18 (2H, m, 1 × H of 2 × CH_2), 2.21 (1H, d, *J* 15.9 Hz, 1 × H of CH_2P), 2.27 (1H, d, *J* 15.9 Hz, 1 × H of CH_2P), 2.36–2.64 (3H, m, 1 × H of CH_2 and CH_2), 4.06 (4H, m, 2 × CH_2 of POEt), 4.54 (1H, br s, OH), 7.45 (2H, dt, *J* 1.5 and 7.1 Hz, 3′-H and 5′-H), 7.56 (1H, tt, *J* 1.2 and 7.2 Hz, 4′-H) and 7.99 (2H, dd, *J* 1.2 and 8.4 Hz, 2′-H and 6′-H); **^{13}C-NMR** (75.0 MHz, $CDCl_3$) 16.3 (dd, J_{CP} 2.7

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cl1	1.03058(7)	0.81968(8)	0.30756(6)	0.0453(2)
O1	0.78757(19)	1.0592(2)	0.20686(13)	0.0431(5)
O2	0.60668(17)	1.03214(17)	0.41117(13)	0.0289(4)
H1	0.620(3)	1.025(3)	0.462(2)	0.039(9)*
O3	0.35600(18)	0.9756(2)	0.42174(13)	0.0390(5)
O4	0.42857(19)	0.7713(2)	0.37031(15)	0.0441(5)
O5	0.37216(19)	0.9643(2)	0.25892(13)	0.0451(6)
P1	0.42617(7)	0.91247(7)	0.34881(5)	0.03158(19)
C1	0.8757(2)	1.1090(2)	0.31327(18)	0.0281(6)
C2	0.9190(3)	1.2041(3)	0.2512(2)	0.0367(7)
H2	0.9081	1.2184	0.1905	0.044*
C3	0.9775(3)	1.2776(3)	0.2773(2)	0.0429(8)
H3	1.0070	1.3416	0.2346	0.051*
C4	0.9926(3)	1.2573(3)	0.3658(2)	0.0424(8)
H4	1.0331	1.3072	0.3838	0.051*
C5	0.9492(3)	1.1648(3)	0.4279(2)	0.0380(7)
H5	0.9591	1.1520	0.4887	0.046*
C6	0.8909(2)	1.0899(3)	0.40233(18)	0.0311(6)
H6	0.8616	1.0261	0.4454	0.037*
C7	0.8161(2)	1.0308(3)	0.28143(17)	0.0285(6)
C8	0.7910(2)	0.9139(2)	0.34242(17)	0.0261(6)
C9	0.8790(2)	0.8147(3)	0.35722(19)	0.0313(6)
C10	0.8641(3)	0.6936(3)	0.4145(2)	0.0410(7)
H10A	0.9005	0.6797	0.4692	0.049*
H10B	0.9078	0.6274	0.3812	0.049*
C11	0.7299(3)	0.6895(3)	0.4407(2)	0.0413(7)
H11A	0.7198	0.6215	0.4924	0.050*
H11B	0.7011	0.6736	0.3901	0.050*
C12	0.6526(3)	0.8103(3)	0.46569(18)	0.0338(6)
H12A	0.5670	0.8027	0.4871	0.041*
H12B	0.6830	0.8274	0.5151	0.041*
C13	0.6572(2)	0.9165(2)	0.38572(17)	0.0263(6)
C14	0.5851(2)	0.9142(3)	0.31363(17)	0.0290(6)
H14A	0.6256	0.8408	0.2872	0.035*
H14B	0.5917	0.9868	0.2654	0.035*
C15	0.3125(4)	0.7355(4)	0.4116(3)	0.0727(12)
H15A	0.2930	0.7442	0.4751	0.087*
H15B	0.2462	0.7908	0.3804	0.087*
C16	0.3190(4)	0.6118(4)	0.4066(3)	0.0748(13)
H16A	0.3441	0.6018	0.3441	0.112*
H16B	0.2387	0.5924	0.4296	0.112*
H16C	0.3786	0.5564	0.4427	0.112*
C17	0.2574(3)	1.0520(4)	0.2536(2)	0.0527(9)
H17A	0.2503	1.1146	0.2893	0.063*
H17B	0.1891	1.0101	0.2784	0.063*
C18	0.2510(4)	1.1109(4)	0.1596(2)	0.0668(12)
H18A	0.3192	1.1517	0.1352	0.100*
H18B	0.1738	1.1716	0.1559	0.100*
H18C	0.2559	1.0489	0.1249	0.100*
Cl1A	1.32032(7)	0.72983(7)	0.15285(6)	0.0423(2)
O1A	1.12185(18)	0.50762(19)	0.28351(13)	0.0371(5)
O2A	1.05677(18)	0.48866(17)	0.08935(13)	0.0290(4)
H1A	1.105(3)	0.478(3)	0.043(3)	0.056(11)*
O3A	0.78414(19)	0.5752(2)	0.06055(16)	0.0533(7)
O4A[a]	0.7399(3)	0.7731(2)	0.1049(3)	0.0454(11)
O4B[b]	0.6684(3)	0.7317(3)	0.1629(2)	0.0370(15)
P1A	0.78278(7)	0.62847(7)	0.13530(5)	0.0347(2)
C1A	1.3059(2)	0.4317(2)	0.19283(18)	0.0295(6)
C2A	1.3536(3)	0.3493(3)	0.2649(2)	0.0397(7)
H2A	1.3099	0.3500	0.3240	0.048*
C3A	1.4640(3)	0.2666(3)	0.2510(2)	0.0489(9)
H3A	1.4964	0.2113	0.3005	0.059*
C4A	1.5268(3)	0.2646(3)	0.1651(3)	0.0502(9)
H4A	1.6028	0.2081	0.1557	0.060*
C5A	1.4802(3)	0.3442(3)	0.0926(2)	0.0440(8)
H5A	1.5231	0.3411	0.0336	0.053*
O5A[a]	0.6929(3)	0.5995(3)	0.22647(18)	0.0511(12)
O5B[b]	0.7742(4)	0.5107(4)	0.2121(3)	0.060(2)
C6A	1.3702(3)	0.4287(3)	0.1062(2)	0.0349(7)
H6A	1.3389	0.4845	0.0565	0.042*
C7A	1.1878(2)	0.5194(2)	0.21040(18)	0.0277(6)
C8A	1.1467(2)	0.6242(2)	0.13589(17)	0.0245(6)
C9A	1.1967(2)	0.7207(3)	0.10722(19)	0.0294(6)
C10A	1.1584(3)	0.8301(3)	0.0367(2)	0.0373(7)
H10C	1.2228	0.8305	−0.0169	0.045*
H10D	1.1489	0.9056	0.0595	0.045*
C11A	1.0387(3)	0.8293(3)	0.0105(2)	0.0379(7)
H11C	1.0300	0.8839	−0.0485	0.045*
H11D	0.9697	0.8610	0.0551	0.045*
C12A	1.0341(3)	0.6995(2)	0.00547(18)	0.0292(6)
H12C	0.9579	0.7023	−0.0154	0.035*
H12D	1.1037	0.6676	−0.0387	0.035*
C13A	1.0395(2)	0.6133(2)	0.09632(17)	0.0250(6)
C14A	0.9216(2)	0.6385(3)	0.16439(19)	0.0336(7)
H14C	0.9104	0.7218	0.1759	0.040*
H14D	0.9338	0.5802	0.2214	0.040*
C15A[a]	0.6118(3)	0.8303(3)	0.0940(2)	0.0491(9)
H15C[a]	0.5566	0.8097	0.1509	0.059*
H15D[a]	0.5894	0.8000	0.0469	0.059*
C15B[b]	0.6118(3)	0.8303(3)	0.0940(2)	0.0491(9)
H15E[b]	0.5257	0.8642	0.1179	0.059*
H15F[b]	0.6135	0.7976	0.0405	0.059*
C16A[a]	0.6003(5)	0.9663(3)	0.0682(4)	0.0441(14)
H16D[a]	0.5158	1.0068	0.0611	0.066*
H16E[a]	0.6545	0.9858	0.0116	0.066*
H16F[a]	0.6230	0.9952	0.1152	0.066*
C16B[b]	0.6830(8)	0.9282(7)	0.0697(5)	0.059(3)
H16G[b]	0.6475	0.9946	0.0240	0.088*
H16H[b]	0.7679	0.8938	0.0461	0.088*
H16I[b]	0.6802	0.9604	0.1231	0.088*
C17A[a]	0.6375(10)	0.4924(10)	0.2437(3)	0.082(2)
H17C[a]	0.6844	0.4347	0.2041	0.098*
H17D[a]	0.5526	0.5191	0.2315	0.098*
C17B[b]	0.6575(13)	0.4704(19)	0.2400(3)	0.082(2)
H17E[b]	0.6604	0.4014	0.2115	0.098*
H17F[b]	0.5894	0.5386	0.2216	0.098*
C18A[a]	0.6389(4)	0.4309(4)	0.3399(2)	0.0753(13)
H18D[a]	0.5982	0.3623	0.3538	0.113*
H18E[a]	0.5960	0.4899	0.3785	0.113*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H18F[a]	0.7235	0.4002	0.3504	0.113*
C18B[b]	0.6389(4)	0.4309(4)	0.3399(2)	0.0753(13)
H18G[b]	0.5972	0.3628	0.3574	0.113*
H18H[b]	0.5892	0.4997	0.3674	0.113*
H18I[b]	0.7182	0.4043	0.3603	0.113*

[a]Occupancy: 0.604(4); [b]Occupancy: 0.396(4).

and 6.2Hz, CH_3 of POEt), 19.7 (s, CH_2), 33.0 (s, CH_2), 35.5 (s, CH_2), 34.7 (d, J_{CP} 135.3 Hz, CH_2P), 35.6 (s, CH_2), 61.5 (d, J_{CP} 7.0 Hz, $1 \times CH_2$ of POEt), 62.3 (d, J_{CP} 6.1 Hz, $1 \times CH_2$ of POEt), 72.0 (d, J_{CP} 2.7 Hz, C-1), 128.5 (s, C-3' and C-5'), 129.8 (s, C-2' and C-6'), 133.5 (s, C-4′), 133.6 (d, J_{CP} 3.1 Hz, C-3), 136.7 (s, C-1′), 138.5 (d, J_{CP} 16.7 Hz, C-2) and 196.7 (s, C = O); **^{31}P-NMR** ($CDCl_3$) 29.40; **HRMS** (EI): found: 386.1049. $C_{18}H_{24}O_5ClP$ requires' 386.1050. Crystals were obtained by recrystallization from 3:2 ethyl acetate-petroleum ether mixture.

Experimental details

Hydrogen atoms were located from the difference map then positioned geometrically and allowed to ride on their respective parent atoms. Hydrogen atoms involved in hydrogen bonding were located from the difference map and refined freely. Two ethoxy groups made up of atoms O4A, C15A and C16A and O5A, C17A and C18A were found to be disordered. These were refined over two positions with the final occupancies over the two positions being 0.604(4) and 0.396(4), respectively.

Discussion

Owing to the importance of cycloalkenones as chemical units in a large number of naturally occurring substances [5], development of new synthetic methods leading to substituted derivatives is currently one focal point in synthetic organic chemistry [6].

Lithiated diethyl alkylphosphonates react with 3-chlorocyclohex-2-en-1-ones substituted with a benzoyl group at the 2-position to afford the 1-(diethoxy phosphonomethyl) 2-benzoyl-3-chloro-2-cyclohexen-1-ol. This compound could be purified by column chromatography and its melting point determined without any signs of decomposition. The related adduct of trimethylsilylmagnesium bromide, on the other hand, previously fragmented spontaneously *in situ* to yield a diene [7–9].

The crystal structure contains two molecules in the asymmetric unit – one ordered and the other disordered around the ethoxy groups (*cf.* the figure). O-H···O = P intermolecular hydrogen bonding occurs between adjacent molecules forming a hydrogen bonded pair of centrosymetrically related molecules for both crystallographically independent molecules (graph set descriptor: $R^2_2(12)$). Ordered molecules form hydrogen bonds exclusively to the other ordered molecules whereas disordered molecules form hydrogen bonds to the other disordered molecules.

Bond lengths and angles are all in the expected ranges.

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