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2-[Dichloro(phenoxy)methyl]phenyl dichlorophosphonate

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Key indicators

Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.002 Å
R factor = 0.024
wR factor = 0.065
Data-to-parameter ratio = 16.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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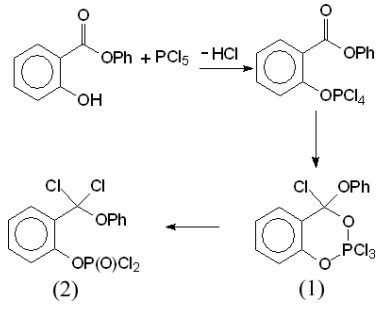
The reaction of phosphorus pentachloride with phenyl salicylate yielded a compound of chemical formula $C_{13}H_9Cl_4O_3P$, which was originally thought to contain a P—O—C heterocycle. The true molecular structure has now been established by the determination of its crystal structure. There are two molecules in the asymmetric unit.

Comment

In previous studies (Pinkus *et al.*, 2004), it was shown that products with unusual structures were formed from the reaction of 2-hydroxybenzophenones with phosphorus pentachloride, whereas ordinary phenols reacted only to give unstable hygroscopic products $ArOPCl_4$ (Anschütz & Emery, 1887, 1889). It was of interest to see whether 2-hydroxyphenolic esters would behave similarly.

Phenyl salicylate undergoes a reaction with phosphorus pentachloride to form a phosphorylated product, the carbonyl oxygen of which has been substituted by Cl atoms, in a manner that has been described previously (Pinkus & Waldrep, 1962). The progress of the reaction proceeds, as shown in the scheme, through the initial loss of one equivalent of HCl. At this point, the moisture-sensitive tetrachlorinated intermediate undergoes an intramolecular chlorination at the carbonyl to leave a six-membered heterocycle that was initially thought to be the final reaction product. Initial spectroscopic data, which included an IR P—O stretching region that was cluttered, even in the starting material, were inconclusive regarding the structure of the final product. Given that P—O—C heterocycles of the type that would be plausible here had been previously demonstrated (Cade & Gerrard, 1954; Young, 1952), the cyclic structure, (1), was thus accepted as true, though not entirely ruling out a dichlorinated phosphorus oxide product. It is now known, as demonstrated here by crystallography, that the chlorination of the carbonyl C atom proceeds a step further, to leave a CCl_2 group and a terminally bound phosphorus oxide, neither of which is involved in the formation of a ring, thus yielding the title compound, (2).



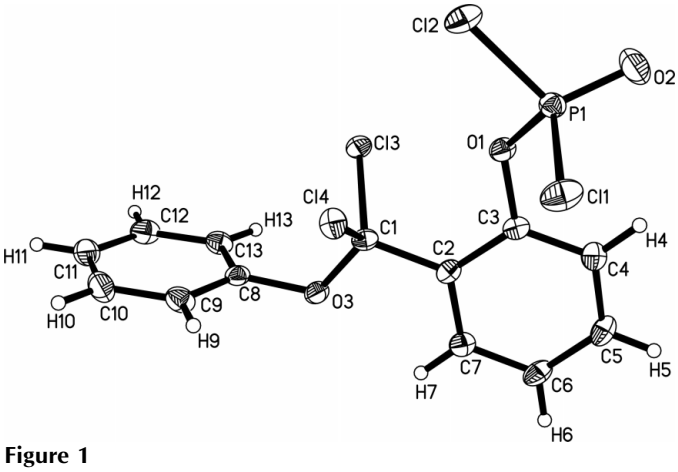


Figure 1
The structure of one of the molecules of the asymmetric unit of (2), with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

The molecular structure of (2) (Fig. 1) shows bond lengths and angles that are comparable with those of other dichlorophosphinic acids and α-dichloroethers. The two rings of the structure are nearly perpendicular, to decrease their interaction with the bulky CCl_2 linker. Furthermore, it is also a result of this centralized bulk that a widening of the C1—O3—C8 angle to 120.08 (11) occurs, along with a shift of atom O3 out of the plane of the ring atoms C8–C13. The P—Cl2 vector bisects the angle Cl3—C1—Cl4.

Interatomic interaction in (2) is limited to dispersion forces and some rather weak long-distance interactions of the P-bound oxide with ring H atoms of adjacent molecules. It should also be noted that there are two molecules in the asymmetric unit; they differ only in the orientation of the $OP(O)Cl_2$ substituents

Experimental

Compound (2) was prepared by the dropwise addition of phenyl salicylate (42.3 g, 198 mmol) in dry benzene (75 ml) to a solution of phosphorus pentachloride (41.1 g, 197 mmol) in benzene (75 ml). The HCl which evolved from the reaction was collected in a sodium hydroxide trap separated from the reaction vessel by a calcium chloride tube. After stirring for 15 min, the solvent was removed *in vacuo* to yield 76.2 g (100%) of (2) as a white solid. Analytical purity was obtained by recrystallization from isopropyl ether. Crystals for X-ray analysis were grown by dissolving the compound in hot *n*-hexane and allowing the solution to cool slowly.

Crystal data

$C_{13}H_9Cl_4O_3P$
M_r = 385.97
Orthorhombic, *Pbca*
a = 13.9369 (14) Å
b = 19.0631 (17) Å
c = 23.503 (2) Å
V = 6244.2 (10) Å^3
Z = 16
D_x = 1.642 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7002 reflections
θ = 2.5–28.5°
μ = 0.87 mm^{-1}
T = 110 (2) K
Block, colorless
0.24 × 0.20 × 0.20 mm

Data collection

Bruker X8 APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.816, T_{max} = 0.838
107 431 measured reflections
6382 independent reflections
5384 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 26.4°
$h = -17 \rightarrow 17$
$k = -19 \rightarrow 23$
$l = -29 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.065
S = 1.02
6382 reflections
379 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0307P)^2 + 3.3409P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—P1	1.9897 (6)	O2—P1	1.453 (1)
Cl2—P1	1.9935 (6)	O3—C1	1.383 (2)
O1—P1	1.572 (1)	O3—C8	1.422 (2)
C1—O3—C8	120.08 (11)		

H atoms were included in calculated positions (C—H = 0.930 Å) and treated as riding, with U_{iso}(H) = 1.2U_{iso}(C).

Data collection: *APEX*2 (Bruker, 2003); cell refinement: *APEX*2; data reduction: *SAINT-Plus* (Bruker, 2003); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL*.

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