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α,α,4-Trichloro-α-phenyl-*o*-tolyl dichlorophosphinate

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Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.002 Å
R factor = 0.025
wR factor = 0.071
Data-to-parameter ratio = 25.5

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

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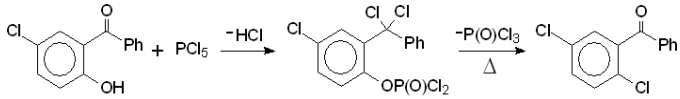
The reaction of 5-chloro-2-hydroxybenzophenone with phosphorus pentachloride yielded the title compound, $C_{13}H_8Cl_5O_2P$. This compound can then be decomposed into a 2,5-dichlorobenzophenone by heating. There are two molecules of the title compound in the asymmetric unit.

Comment

In general, phenols are known to react with phosphorus pentachloride to form moisture-sensitive products having a $PhOPCl_4$ type of structure (Anschütz & Emery, 1887, 1889). It has recently been demonstrated (Pinkus *et al.*, 2004*a*,*b*) that 2-hydroxyphenolic esters undergo a different sort of reaction that produces a relatively moisture-stable product. In this reaction, the carbonyl O atom is exchanged for two Cl atoms to form a dichloromethylene and an $OP(O)Cl_2$ group. On the basis of spectroscopic evidence, this reaction was also reported to occur when 5-chloro-2-hydroxybenzophenone was reacted with PCl_5 (Pinkus, Ma *et al.*, 2004, and references therein).



(I)

It is definitively shown here, by its crystal structure, that the reaction product is indeed analogous to those of the 2-hydroxyphenolic ester reactions. Compound (I) was obtained by reaction of 5-chloro-2-hydroxybenzophenone with PCl_5, giving off an equivalent of HCl for each equivalent of benzophenone, as shown in the scheme. It has also been

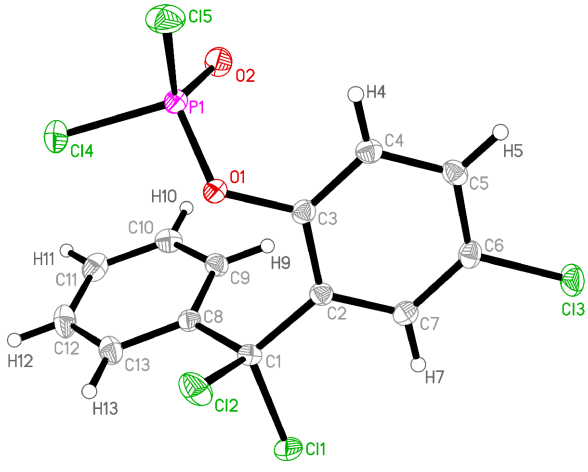


Figure 1
The molecular structure of one of the molecules of the asymmetric unit of (I), with displacement ellipsoids drawn at the 50% probability level

shown that upon heating, loss of $P(O)Cl_3$ occurs leaving a 2,5-dichlorinated benzophenone (Pinkus, Klausmeyer *et al.*, 2004), making the title compound a convenient intermediate en route to 2-chlorobenzophenones.

The molecular structure of (I) (Fig. 1) shows bond lengths and angles typical of aromatic chlorohydrocarbon atoms. There are two molecules of (I) in the asymmetric unit, showing slight differences in bond lengths and angles about the rings and a twisting of the $OP(O)Cl_2$ substituent.

Experimental

Compound (I) was prepared as reported in Pinkus & Meng (1966) by reaction of 5-chloro-2-hydroxybenzophenone with phosphorus pentachloride. Single crystals of (I) were obtained by cooling of a hot cyclohexane solution.

Crystal data

$C_{13}H_8Cl_5O_2P$
M_r = 404.41
Triclinic, $P\overline{1}$
a = 9.5227 (7) Å
b = 10.2195 (7) Å
c = 17.5587 (12) Å
α = 73.238 (4)°
β = 75.348 (4)°
γ = 87.593 (4)°
V = 1582.07 (19) Å^3
Z = 4
D_x = 1.698 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7462 reflections
θ = 2.3–30.4°
μ = 1.02 mm^{-1}
T = 273 (2) K
Block, colorless
0.21 × 0.17 × 0.13 mm

Data collection

Bruker APEX2 CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.817, T_{max} = 0.879
61 218 measured reflections
9669 independent reflections
8283 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 30.6°
$h = -13 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.071
S = 1.06
9669 reflections
379 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0369P)^2 + 0.3855P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.58 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl6—C14	1.8132 (11)	Cl2—C1	1.8070 (12)
P1—O2	1.4576 (9)	P2—O4	1.4524 (10)
P1—O1	1.5830 (9)	P2—O3	1.5699 (9)
P1—Cl4	1.9836 (4)	P2—Cl9	1.9838 (5)
P1—Cl5	1.9948 (4)	P2—Cl10	1.9917 (5)
Cl1—C1	1.8123 (12)		
C3—O1—P1	122.67 (7)	C21—C14—C15	113.26 (9)
C16—O3—P2	127.64 (8)	C8—C1—C2	114.14 (9)

H atoms were included in calculated positions (C—H = 0.93 Å); isotropic displacement parameters were fixed [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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