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Key indicators

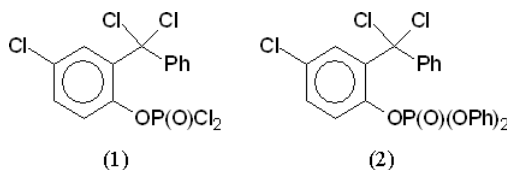
Single-crystal X-ray study
 $T = 273$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.028
 wR factor = 0.073
Data-to-parameter ratio = 15.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Diphenyl 2-($\alpha,\alpha,4$ -trichlorobenzyl)phenyl phosphateThe reaction of $\alpha,\alpha,4$ -trichloro- α -phenyl-*o*-tolyl dichlorophosphinate with phenol leads to the selective substitution of the phosphorus-bound chlorines by OPh groups. The product, 4-chloro-(α,α -dichlorobenzyl)phenyl diphenyl phosphate, $\text{C}_{25}\text{H}_{18}\text{Cl}_3\text{O}_4\text{P}$, has a CCl_2 group that remains intact.

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Comment

 $\alpha,\alpha,4$ -Trichloro- α -phenyl-*o*-tolyl dichlorophosphinate, (1), was formed by loss of HCl from the reaction of 4-chlorophenyl 2-hydroxybenzophenone and phosphorus pentachloride (Pinkus *et al.*, 2004). This is in contrast to the PhOPCl_4 type of product expected from the reactions of phenols and phosphorus pentachloride (Anschütz & Emery, 1887, 1889). The further reaction of (1) with phenol was carried out to obtain the compound shown as structure (2). This compound has proven to be more stable to hydrolysis than previously prepared compounds (Pinkus *et al.*, 2004*a,b*) in testing for anticancer activity.2,4,6-Collidine was the best base for the reaction of (1) and phenol; it yielded a purer product and also a higher yield. Less satisfactory results were obtained with triethylamine, pyridine, or 1,4-diazabicyclo[2.2.2]octane. The molecular structure of (2) is displayed in Fig. 1. The three (C)O–P–O(C) bond angles (Table 1) range from 100.85 (6) to 102.59 (6)°, while the (C)O–P–O angles range from 115.68 (7) to 117.52 (7)°. This is comparable to the angles of triphenyl phosphate (Davies & Stanley, 1962) which are in the ranges 100.7–108.2 and 113.6–117.1° for the corresponding (C)O–P–O(C), and (C)O–P–O measurements, respectively. In addition, the change from the PCl_2 of (1) to the P(OPh)_2 of (2) results in only minor changes to bond lengths and angles of the structure. The remaining bond lengths and angles are typical of aromatic chlorohydrocarbons. Selected bond lengths and angles are displayed in Table 1.

Experimental

 $\alpha,\alpha,4$ -Trichloro- α -phenyl-*o*-tolyl dichlorophosphinate, (1), was obtained by reaction of phosphorus pentachloride with phenyl salicylate as previously described (Pinkus *et al.*, 2004). For the synthesis of diphenyl 2-($\alpha,\alpha,4$ -trichlorobenzyl)phenyl phosphate, (2),

a solution of phenol (12.7 g, 0.135 mol) in benzene (70 ml) was added dropwise with stirring to a solution of $\alpha,\alpha,4$ -trichloro- α -phenyl-*o*-tolyl dichlorophosphinate (27.3 g, 0.0675 mol) and dried redistilled 2,4,6-collidine (16.4 g, 0.0135 mol) in benzene (100 ml). After addition was complete, the mixture was stirred for a further 2 h. Collidine hydrochloride which had precipitated was collected by filtration and the solvent was removed from the filtrate *in vacuo*, during which time more collidine hydrochloride precipitated and was removed by filtration. The product was a colorless viscous liquid which crystallized on seeding as a white solid (33.4 g, 95.2% yield). After three recrystallizations from cyclohexane, large white crystals were obtained (m.p. 349.0–349.8 K). Analysis (Geller Labs, Bardonia, NY) calculated for $C_{25}H_{18}Cl_3O_4P$: C 57.76, H 3.49, Cl 20.47, P 5.96%; found: C 58.17, H 3.65, Cl 20.02, P 5.61%. The IR spectrum (CCl_4) showed no CO stretching band but had a PO stretching band at 1294 cm^{-1} . Other bases (pyridine, triethylamine, and 1,4-diazabicyclo[2.2.2]octane) were less satisfactory than the one used above. X-ray quality crystals were obtained by recrystallization from cyclohexane.

Crystal data

$C_{25}H_{18}Cl_3O_4P$
 $M_r = 519.71$
 Triclinic, $P\bar{1}$
 $a = 9.452$ (4) Å
 $b = 9.629$ (5) Å
 $c = 15.136$ (5) Å
 $\alpha = 74.051$ (18)°
 $\beta = 79.192$ (12)°
 $\gamma = 60.608$ (10)°
 $V = 1151.7$ (9) Å³

$Z = 2$
 $D_x = 1.499\text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 6521 reflections
 $\theta = 2.5$ – 29.1 °
 $\mu = 0.50\text{ mm}^{-1}$
 $T = 273$ (2) K
 Block, colorless
 $0.24 \times 0.19 \times 0.14\text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.890$, $T_{\max} = 0.932$
 17223 measured reflections

4640 independent reflections
 3989 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$
 $\theta_{\text{max}} = 26.4$ °
 $h = -11 \rightarrow 11$
 $k = -12 \rightarrow 12$
 $l = -18 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.073$
 $S = 1.09$
 4640 reflections
 298 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0262P)^2 + 0.4371P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.33\text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.36\text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

P1—O2	1.4546 (13)	P1—O3	1.5655 (13)
P1—O4	1.5635 (13)	P1—O1	1.5873 (12)
O2—P1—O4	116.24 (7)	O2—P1—O1	115.68 (7)
O2—P1—O3	117.52 (7)	O4—P1—O1	101.46 (7)
O4—P1—O3	102.59 (6)	O3—P1—O1	100.85 (6)

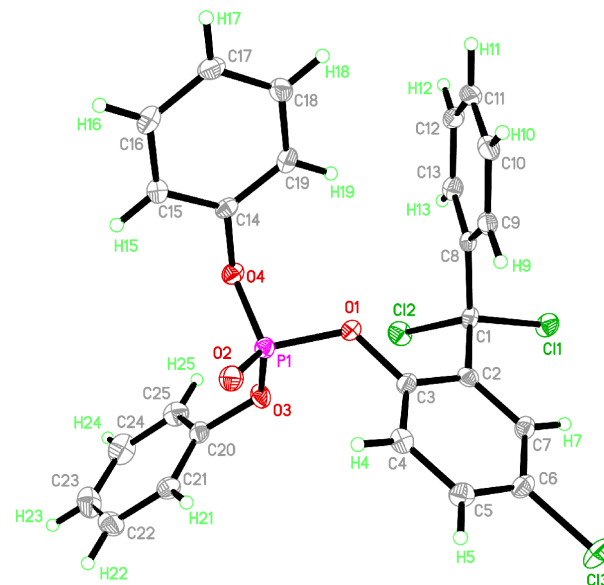


Figure 1

A view of the molecular structure of (2); displacement ellipsoids are drawn at the 50% probability level.

H atoms were included in calculated positions ($C-H = 0.93$ Å) and made to ride, with $U_{\text{iso}}(H) = 1.2U_{\text{iso}}(C)$.

Data collection: *APEX2* (Bruker, 2003); cell refinement: *APEX2*; data reduction: *SAINTE-Plus* (Bruker, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL*.

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