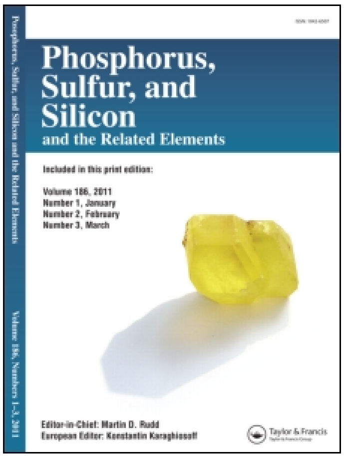

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A Convenient One-Pot Synthesis of Di-*t*-butylphosphinic Chloride

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A Convenient One-Pot Synthesis of Di-*t*-butylphosphinic Chloride

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A convenient one-pot synthesis of $(\text{t-}Bu)_2P(O)Cl$ *(**1**) from m-chloroperbenzoic acid and* $(\text{t-}Bu)_2PCl$ *is described. The byproduct m-chlorobenzoic acid is neutralized by addition of* Et_3N*. Complex **1** crystallizes in the monoclinic space group* $P2_1/c$ *(No. 14), with* $a = 5.9637(2)$ Å, $b = 11.4734(4)$ Å, $c = 16.2400(5)$ Å *and* $\beta = 107.7160(14)$*.*

Keywords Chemical synthesis; crystal structure; phosphinic chloride

INTRODUCTION

Organophosphorus compounds have extensive applications in the field of chemistry, especially in the area of catalysis. Trivalent phosphorous compounds are widely employed as ligands in several important homogeneously catalyzed processes.[1,2] Phosphine oxides can also be useful ligands to metal centers, particularly in combination with phosphines.[3] Mixed phosphines, with various combinations of alkyl groups, are often prepared from dialkylphosphines or the corresponding phosphides. These, in turn, can be derived from the corresponding dialkylphosphine halides by various reduction procedures. The P–Cl bonds in trivalent phosphorous compounds such as dialkylphosphine chlorides are very sensitive to hydrolysis.[4] To clarify the structure and nomenclature, relevant phosphorus compounds are shown in Scheme 1. Oxidation affords the dialkyl phosphinic chlorides, which are much more stable with respect to hydrolysis. Dialkylphosphinic chlorides, specifically the dimethyl compound $(Me)_2P(O)Cl$ have proven to be useful acid stable protecting groups for the side chain phenol moiety of tyrosine in peptide synthesis.[5–7]

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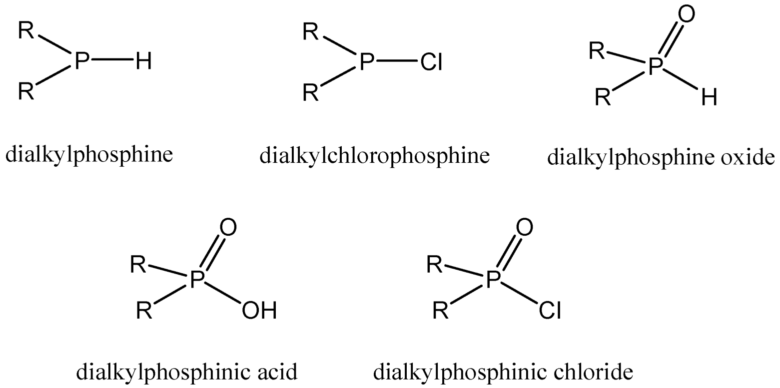


SCHEME 1

In recent years, the use of sterically demanding alkyl phosphine ligands in homogeneous catalysis has increased. Various aryl(di-*t*-butyl)phosphine ligands have found numerous applications, especially for Pd mediated cross-coupling reactions.[6–8] In our own research, we have employed pincer ligands containing a di-*t*-butylphosphinite moiety.[9–11] In particular, we found that a (POCOP)Ir(H)$_2$ (POCOP = [κ^3-1,3-(OP(t-Bu)$_2$)$_2$C$_6$H$_3$]) complex is an exceptionally active catalyst for the dehydrogenation of NH_3BH_3.[11]

Synthesis of tertiary butyl phosphine derivatives often requires the use of reagents such as (t-Bu)$_2$PCl, (t-Bu)$_2$PH, and the corresponding phosphide anion. These are very reactive species, with restrictions on air transport due to facile oxidation and hydrolysis reactions.[4] However, the oxy-chloride analogue, (t-Bu)$_2$P(O)Cl is an air stable compound. We report herein a simple, high-yield synthesis and purification method for di-*t*-butylphosphinic chloride, **1**, (t-Bu)$_2$P(O)Cl). This phosphinic chloride is indefinitely stable on the benchtop and can be converted to useful reagents such as the phosphine (t-Bu)$_2$PH or back to the chlorophosphine by well established methods.[12–14]

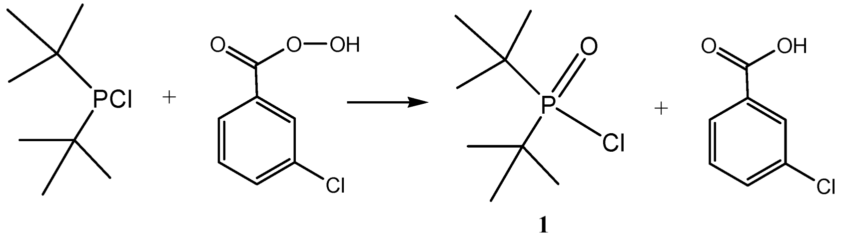
RESULTS AND DISCUSSION

While several syntheses have been reported for the title compound, we found them to suffer from low yields and difficult purification procedures.[15–19] One such report describes the synthesis of **1** from di-*t*-butylchlorophosphine using aqueous hydrogen peroxide as the oxidant.[15] This is surprising, since dialkylchlorophosphines are well known to rapidly hydrolyze to give HCl and the corresponding phosphine oxide.[4] In our hands, we found that reaction of (t-Bu)$_2$PCl with aqueous hydrogen peroxide affords a complex mixture of products, with the major product being di-t-butylchlorophosphine oxide (t-Bu)$_2$P(O)H, which is readily identified by ^{1}H and ^{31}P NMR spectroscopy (δ P-H, 5.82 ppm, $J_{PH} = 422$ Hz and δ (P) = 63.5 ppm).[20] The oxide was also observed if glassware used in reactions of (t-Bu)$_2$PCl was not rigorously dried.

Another synthetic method described the vigorous bubbling of O_2 through a refluxing xylene solution of (t-Bu)$_2$PCl.[15] We found this reaction to give only partial oxidation, affording (t-Bu)$_2$PCl, (t-Bu)$_2$P(O)Cl, and (t-Bu)$_2$P(O)H in the ratio 80:15:5.

A four-step synthesis has also been reported in which the chlorophosphine is hydrolyzed to the oxide, oxidized to the phosphinic acid, followed by chlorination with thionyl chloride to the give the title compound **1**.[16,17] However, we found that the oxidation step proceeded in low yield; therefore, we did not pursue this pathway.

The method outlined below in Scheme 2 starts with the commercially available (t-Bu)$_2$PCl. Reaction with m–CPBA at 0°C generates **1** in along with byproduct *meta*-chlorobenzoic acid. An excess of triethylamine is then added to deprotonate the benzoic acid. The entire reaction mixture is eluted down a silica plug (2 grams) with methylene chloride/hexanes (2:1). The volatiles (solvent and excess NEt$_3$) are removed, leaving behind colorless crystalline compound **1** in ~95% yield.



1

SCHEME 2

Structure of 1

Crystals of **1** suitable for X-ray diffraction were grown by concentration of a methylene chloride solution. A clear prism of dimensions 0.59 × 0.29 × 0.12 mm was mounted on a glass capillary with oil. Data was collected at 130 K. Crystal-to-detector distance was 30 mm and exposure time was 20 s per degree for all sets. The scan width was 2°. Data

TABLE I Crystallographic Data for $(t\text{-Bu})_2P(O)Cl$

Empirical formula	$C_8H_{18}ClOP$	
Formula weight	196.66	
Temperature	130 K	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = *5.9637(2)* Å	$\alpha = 90°$.
	b = *11.4734(4)* Å	$\beta = 107.7160(14)°$.
	c = *16.2400(5)* Å	$\gamma = 90°$.
Volume	1058.51 Å^3	
Crystal size	0.59 × 0.29 × 0.12 mm^3	
Index ranges	$-7 \le h \le 7, -14 \le k \le 15, -21 \le l \le 21$	
Reflections collected	22448	
Independent reflections	2522 [R(int) = 0.0824]	
Refinement method	Full-matrix least-squares on F^2	
R final	0.0484	
Goodness-of-fit on F^2	0.984	

collection was 96% complete to 28.3° and 98.2% complete to 25° in ϑ. A total of 22,448 partial and complete reflections were collected covering the indices, h = –7 to 7, k = –14 to 15, l = –21 to 21. 2522 reflections were symmetry independent. Indexing and unit cell refinement indicated a monoclinic P lattice. The space group was $P2_1/c$ (No. 14).

The data was integrated and scaled using hkl-SCALEPACK. Solution by direct methods (SIR97) produced a complete heavy atom phasing model consistent with the proposed structure. All hydrogen atoms

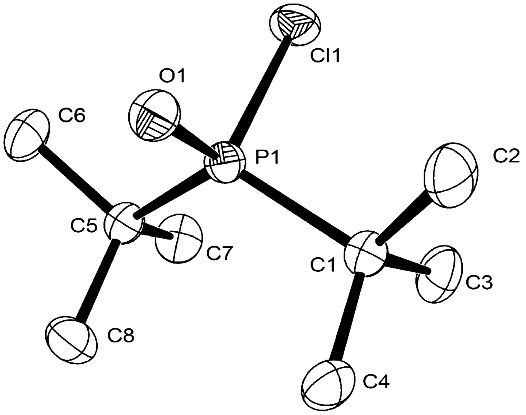
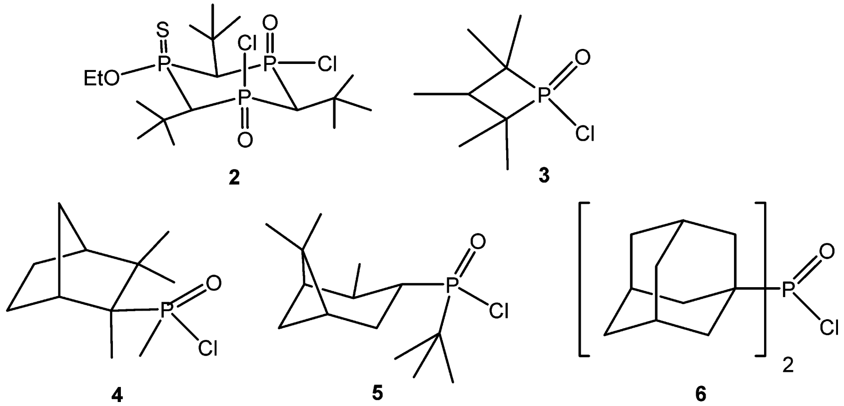


FIGURE 1 ORTEP diagram of [$(t\text{-Bu})_2P(O)Cl$]. 50% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. CCDC deposit number 673,938.

TABLE II Selected Bond Lengths (Å) for $R_2P(O)Cl$ Derivatives

Reference (compound)	P—O	P—Cl	P—C1	P—C2	C—P—C Angle (°)
21 (**2**)	1.477	2.031	1.828	1.837	104.1
22 (**3**)	1.483	2.056	1.834	1.843	85.9
23 (**4**)	1.486	2.051	1.822	1.821	110.2
24 (**5**)	1.463	2.061	1.841	1.872	116.8
25 (**6**)	1.504	2.048	1.840	1.850	103.8
This work (**1**)	1.473	2.068	1.836	1.839	117.7



SCHEME 3

were located using a riding model. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares. The crystallographic data for **1** are tabulated in Table I.

The structure of **1** exhibits some distortions from idealized tetrahedral angles around the central P atom. The ORTEP diagram for **1** is shown in Figure 1. The largest distortion arises from the steric bulk of the t-Bu groups, which leads to a C_1-P-C_5 bond angle of 117.7(3)°. The relevant bond distances are listed in Table II. The bond lengths for this structure fall well within the range of previously reported values.[21–25]

CONCLUSION

Although several methods have been reported for the preparation of **1**, none of the existing procedures is satisfactory. The method reported here provides a simple one-pot synthesis and isolation procedure that should be general for a wide variety of R groups.

EXPERIMENTAL

General Procedures

Benzene was distilled from CaH_2. All other solvents were reagent grade and were used as received. Di-*t*-butylchlorophosphine and all other reagents were supplied by Aldrich. Glove-box and standard Schlenk techniques were used as required. NMR spectra were obtained at ambient temperature on Bruker AV300 and AV500 spectrometers, with chemical shifts (δ) reported in ppm downfield of tetramethylsilane. ^{31}P NMR spectra were referenced externally to 85% H_3PO_4. Elemental analyses were performed by Desert Analytics, Phoenix, AZ.

Abbreviations

Di-*t*-butylphosphinic chloride = $(t\text{-Bu})_2P(O)Cl$; PMHS = polymethylhydrosilane; *m*-CPBA = *meta*-chloroperbenzoic acid.

Synthesis of Di-*t*-butylphosphinic Chloride $(t\text{–Bu})_2P(O)Cl$

A Schlenk flask was charged with *m*-CPBA (707 mg, 4.11 mmol) dissolved in CH_2Cl_2 (20 mL). Di-*t*-butylchlorophosphine (0.410 mL, 2.18 mmol) was added dropwise at 0°C. The resulting solution was vigorously stirred for 1 h at room temperature. Neat triethylamine (~1 mL, 7.2 mmol) was added dropwise, and the solution was allowed to stir for 20 min. The entire reaction mixture was chromatographed on a silica plug (2 grams), eluting with methylene chloride. Evaporation of the solvent gave 0.402 g of a white crystalline solid. (94% yield) Anal. calcd. for $POClC_8H_{18}$: C, 48.85; H, 9.22. Found: C, 48.84; H, 8.79. ^1H NMR (500 MHz, C_6D_6): 1.37 (d, 18 H, -CH_3, $J = 17$ Hz). ^{13}C NMR: 41.74 (d, P-C-$(CH_3)_3$, $J = 62$ Hz), 26.9 (s, -CH_3). ^{31}P NMR: $\delta(P) = 96.2$ (s).

Supplementary Material

Crystallographic data for the structural analysis of compound **1** has been deposited at the Cambridge Crystallographic Data Center (CCDC number 673938). Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223-336033; email: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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