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A Functionalized Alkyldiphenylphosphine as an Efficient and Mild Reagent in CCl_4-Promoted Substitution Reactions: Kinetics and Mechanism of the Reaction in $CHCl_3$

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(Pyrid-2-ylethyl)diphenylphosphine [$(C_5H_4NCH_2CH_2)PPh_2$] can be used at 35–45 °C in carbon tetrachloride–chloroform to give high yields of primary and secondary alkyl chlorides from the corresponding alcohols. The isolation of products is simplified by removal of the phosphorus-containing products by extraction into a dilute aqueous acid solution. The complex reaction was studied by ^{31}P NMR. The rate constants based on the decay of phosphine are reported. The rapid conversion of alcohols proceeds equally via chlorination by $[(C_5H_4NCH_2CH_2)PPh_2Cl]CCl_3$ (path A) and by $[(C_5H_4NCH_2CH_2)PPh_2Cl]Cl$ (path B). The rates of formation and decay of an isobutoxyphosphonium intermediate, $[(i\text{-}C_4H_9O)(C_5H_4NCH_2CH_2)PPh_2]Cl$, have been measured with ^{31}P NMR.

Introduction

The triphenylphosphine–carbon tetrachloride reagent has found widespread applications in chlorination, condensation, esterification, and dehydration reactions.[1-3] The reagent is attractive except that the reactions are often carried out at reflux temperatures and the phosphorus-containing reaction products are difficult to remove. Recently, improvements in both reaction times and product isolation have been reported with the use of polystyrene polymer supported phosphine resins.[4-6] It has been postulated that the improvements obtained with the polymer-supported resins were due to the interactions between the neighboring phosphine groups. We felt that bifunctional tertiary phosphines would offer similar benefits. Therefore, we decided to investigate the chlorination of primary and secondary alcohols with CCl_4 and the solid bifunctional alkyldiphenylphosphines 1,3-bis(diphenylphosphino)propane (DPP) and (pyrid-2-ylethyl)diphenylphosphine (2-PEDP). While both of these phosphines have neighboring groups, the basic pyridyl function in the 2-PEDP reagent molecule permits ready removal of all phosphorus-containing reaction products with an acidic water wash. Thus, these bifunctional phosphine–carbon tetrachloride reagents could offer an extremely attractive alternative for chlorination reactions by optimizing the rate and facilitating halide isolation.

Appel[1] has done extensive work on the mechanisms of the reactions of tertiary phosphine–CCl_4 systems. There are several phosphorus-containing intermediates and products that can be identified by distinctive signals in the ^{31}P NMR spectra. In this manner, we have used ^{31}P NMR to obtain both kinetic and product information.

Results and Discussion

Preparation of Alkyl Chlorides. A variety of alcohols were treated with the bifunctional phosphines DPP and 2-PEDP. The monofunctional phosphine ethyldiphenylphosphine (EDP) was used as a control. As shown in Table I, excellent yields of alkyl chlorides were obtained from the primary alcohols 1-octanol, 1-dodecanol, and isobutyl alcohol and the secondary alcohols 2-octanol and 2-dodecanol with each of the alkyldiphenylphosphines with CCl_4 in $CHCl_3$. We have listed primarily the yield data for 2-PEDP in Table I, because the results were virtually identical for all the alkyldiphenylphosphines (e.g., under conditions similar to those listed, the GLC yields of 2-chlorooctane from 2-octanol were 88%, 90%, and 87% with 2-PEDP, DPP, and EDP, respectively). These phosphines react at 35–45 °C, which is a much lower temperature range than was used with any of the previously reported phosphine reagents. The yields are comparable to, and in several instances improved over, those previously reported with other phosphine reagents.[4,5,7-9]

The effect of increased β-branching on the alcohol structure was investigated (Table I). Using DPP–CCl_4 in $CHCl_3$, the reaction with 1-octanol was complete in 1 h at 35 °C, the reaction of isobutyl alcohol required 2 h at 45 °C, and the reaction of neopentyl alcohol was only 35% complete after 38 h at 35 °C. At that time, a large peak at δ 71.9 in the ^{31}P NMR spectrum of the DPP–neopentyl alcohol–CCl_4 reaction mixture revealed that a neopentoxyphosphonium intermediate was present in high concentration and that the intermediate exists an ion pair.[10,11] In the DPP–neopentyl alcohol system, as in the Ph_3P–neopentyl alcohol system, the rate of intermediate formation is many times faster than the rate of intermediate decomposition.[12,13]

With DPP and the cyclic alcohol cyclohexanol only the elimination product cyclohexene was formed. Similarly, it has been reported that polymer-supported phosphines react with cyclohexanol and carbon tetrachloride to give cyclohexene in approximately 50% yield.[4,8]

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Table I. Yields of R′Cl from the Reactions RPPh$_2$ + CCl$_4$ + R′OH

phosphine[a]	substrate	ratio	vol % CCl$_4$	t, °C	time, h	% yield
2-PEDP	1-dodecanol	2:1	15	35	1	97[b]
2-PEDP	1-octanol	2:1	15	35	1	87[c]
2-PEDP	isobutyl alcohol	2:1	15	45	0.55	quant[d]
2-PEDP	2-dodecanol	2:1	15	35	1	90[b]
2-PEDP	2-octanol	2:1	60	30	1.5	88[e,c]
2-PEDP	2-octanol	2:1	100	35	1	33[c]
DPP	neopentyl alcohol	1.2:1	60	60	28.25	35[d]
DPP	cyclohexanol	1.2:1	15	35	2.25	0[d,f]

[a] (Pyrid-2-ylethyl)diphenylphosphine, 2-PEDP; 1,3-bis(diphenylphosphino)propane, DPP. [b] Chloride isolated with ^{1}H NMR and GLC data identical with that of an authentic sample. [c] Yields based on the alcohol determined by GLC analysis with an internal standard. [d] By ^{1}H NMR; integration values based on an internal standard. [e] ^{1}H NMR spectrum of the nonvolatile reaction products showed no signs of remaining alkoxyphosphonium intermediate. [f] Cyclohexene formed quantitatively.

Table II. Kinetic Data Obtained by ^{31}P NMR Spectroscopy for the Reaction RPPh$_2$ + CCl$_4$ + R′OH

RPPh$_2$	concn, M	R′OH	concn, M	vol % CCl$_4$	r[a]	10^4k_{obsd},[b] s^{-1}	% yield path A
			t = 32 °C				
2-PEDP	0.15	2-octanol	0.077	60[c]	0.999	5.83	51
2-PEDP	0.15	2-octanol	0.077	15[d]	0.993	6.53	45
2-PEDP	0.15	2-octanol	0.145	15	0.998	5.26	50
			t = 45 °C				
2-PEDP	0.15	2-octanol	0.075	15	0.999	14.1	41
2-PEDP	0.15	isobutyl alcohol	0.074	15	0.996	15.0	63
2-PEDP	0.15	isobutyl alcohol	0.15	15	0.997	14.6	65
Ph$_3$P	0.17	2-octanol	0.084	16.7	0.995	1.63	0
Ph$_3$P	0.17	isobutyl alcohol	0.083	16.7	0.997	1.64	0

[a] Correlation coefficients, ln [2-PEDP] vs t. number of points for each sequential table entry: 10, 7, 6, 11, 8, 10, 7, 7. [b] Pseudo-first-order rate constants. [c] 6.2 M. [d] 1.55 M.

Recently, there has been considerable interest in polymer-supported phosphine reagents, mainly due to the simplicity of the workup procedure.[4,8] The bifunctional 2-PEDP reagent also offers this distinct advantage; the phosphine-related reaction products are readily extracted from the reaction mixture with an acidic water wash.

Effect of the Neighboring Group on Phosphine Reactivity. The reactions of the acyclic secondary alcohols with each of the three alkyldiphenylphosphines and CCl$_4$ in CHCl$_3$ are essentially complete in 1 h at 35 °C. No neighboring group effect is evident. The main advantages of DPP and 2-PEDP over EDP are practical ones: i.e., they are relatively air-stable solids, and their products are easier to separate from the chlorides formed.

Effect of Solvent. The solvent plays an important role in the phosphine–CCl$_4$ reactions. The rate of the reaction increases with increasing solvating ability of the solvent.[1] Our initial experiments were carried out in CCl$_4$ in order to compare the results with those in the literature.[4] After only 1 h at 35 °C, only 33% of 2-chlorooctane was produced from the 2-PEDP–CCl$_4$–2-octanol reaction mixture, and the phosphorus-containing reaction products began to precipitate. The precipitate was soluble in CHCl$_3$, and it was found that the reaction mixtures remained homogeneous in CHCl$_3$. In the remaining experiments, the phosphine–CCl$_4$–alcohol mixture was dissolved in CHCl$_3$, a solvent that provides more effective solvation[14] of products and also increases the rate of reaction.

A comparison of the reactivity of Ph$_3$P in pure CCl$_4$[4] with that in a 1:2 mixture of CCl$_4$–CHCl$_3$[11] shows that for this phosphine the mixed solvent is essential for a facile reaction. In the polymer-supported phosphines, however, the reverse effect is seen.[4] After 3 h at 60 °C, the yield of 1-chlorooctane is 72% when pure CCl$_4$ is used as solvent and only 45% when a solvent ratio of 1:9 CCl$_4$–CHCl$_3$ is used. Thus, when the reactivity of Ph$_3$P is compared with the reactivity of the polymer-supported phosphines in pure CCl$_4$,[4] the monomer is placed in an unfavorable light. Indeed, we have observed that the reaction of Ph$_3$P with 2-octanol in the CCl$_4$–CHCl$_3$ mixed solvent is complete in 12 h at 45 °C (Table II), whereas in pure CCl$_4$ it is less than 10% complete in 8 h at 60 °C.[4]

Mechanisms of the Reactions. The mechanism of the phosphine–CCl$_4$–alcohol reaction was explored by ^{31}P NMR spectroscopy. The bifunctional phosphine 2-PEDP was chosen over DPP and EDP for these experiments for the following reasons: (1) 2-PEDP is the more attractive reagent due to the ease of chloride product isolation. (2) The ^{31}P NMR spectra are greatly simplified when there is only one phosphorus atom/molecule.

It is well established that the Ph$_3$P–CCl$_4$ reagent converts alcohols into alkyl chlorides by two major pathways,[1,4] which are shown in Scheme I, although Ph$_3$P has been shown to react exclusively by path B under some conditions.[15] In Scheme I are shown five sets of reactions; the first four sets show the reactions that account for the phosphine consumption, and the fifth reaction shows that the two paths have in common the decomposition of the alkoxyphosphonium intermediate **2**, which produces phosphine oxide and alkyl halide.

For the sake of simplicity, path B shows ion pair **3** as arising directly from the reaction of phosphine with CCl$_4$. Alternatively, **3** may form by a rearrangement of the chlorophosphonium trichloromethanide ion pair **1** or by an intramolecular rearrangement of the dipolar complex as well.[1] The active chlorinating agents are considered to be the chlorophosphonium trichloromethanide **1** in path A and the chlorophosphonium chloride **4** in the reactions by path B. The overall reactions are summarized in eq 6–8.

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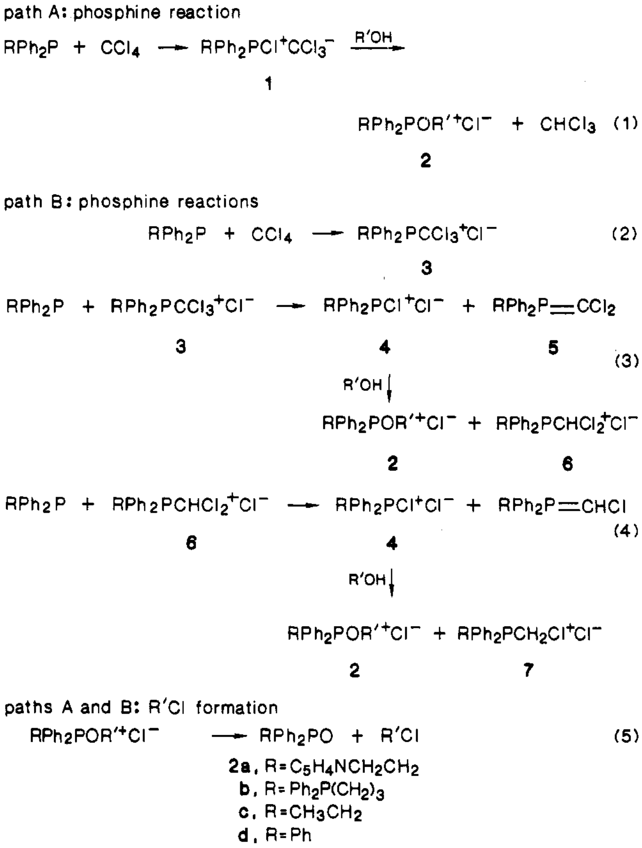
Scheme I. Mechanism of the Reactions of Tertiary Phosphines with CCl_4–R′OH



The overall reactions for path B are summarized in eq 7 and 8. If the reaction proceeds as summarized by eq 7, the stoichiometric ratio of $RPPh_2$ to ROH is 2:1, and if the reaction is summarized by eq 8, the stoichiometry is 3:2. As shown in Scheme I, the reaction written in eq 8 is actually the reaction of salt **6** with R′OH and $RPPh_2$.

path A

$$R'OH + RPPh_2 + CCl_4 \rightarrow R'Cl + RPPh_2O + CHCl_3 \quad (6)$$

path B

$$R'OH + 2RPPh_2 + CCl_4 \rightarrow R'Cl + RPPh_2O + \underset{\mathbf{6}}{RPPh_2CHCl_2{}^{+}Cl^{-}} \quad (7)$$

$$2\,R'OH + 3RPPh_2 + CCl_4 \rightarrow 2\,R'Cl + 2RPPh_2O + \underset{\mathbf{7}}{RPPh_2CH_2Cl^{+}Cl^{-}} \quad (8)$$

The 2-PEDP–CCl_4-promoted chlorination of 2-octanol in $CHCl_3$ was examined kinetically at 32 °C through monitoring the concentrations of the phosphorus-containing species by ^{31}P NMR spectroscopy (Table II). At least a 10-fold molar excess of CCl_4 over phosphine was used so that the dependence of the rate of reaction on the concentrations of the phosphine and alcohol could be observed. Peaks corresponding to the oxide and salt **6a** were evident in the first spectrum, taken an average of 300 s after mixing the reagents; phosphonium salt **7a** appeared after about 1250 s. However, we were unable to observe any buildup and decay of a (oct-2-yloxy)phosphonium intermediate **2a**.[10] The reactions were monitored until complete disappearance of the starting material was noted (over 5 half-lives of reaction). At the end of the reaction, following the disappearance of the last vestiges of the phosphine peak, the phosphorus-containing reaction products consisted of both phosphonium salts **6a** and **7a** and phosphine oxide. The decrease in phosphine followed pseudo-first-order kinetics through 75% of the reaction; the pseudo-first-order rate constant k_{obsd} was 5.9×10^{-4} s^{-1} at 32 °C (Table II). The value of k_{obsd} doubled with a 10 °C rise in temperature. All of the reactions reported in Table II followed pseudo-first-order kinetics. This is a little surprising, since the phosphine reacts not only with CCl_4 but also with intermediates **3** and **6**. The intermediates must first form by the reactions shown in Scheme I before building up to a concentration where they can compete with the CCl_4 for the phosphine.

Table III. NMR Data for 2-PEDP and Derivatives, 32 °C

compound (R = $2\text{-}C_5H_4NCH_2CH_2$)	^{31}P data			
	T_1, s	δ	$^1H'$, δ	J_{HP}, Hz
$RPPh_2$	12.1 ± 2.9	−14.9		
$RP(O)Ph_2$	7.4[a]	31.5		
$[RP(CCl_2H')Ph_2]Cl$[b]	5.8 ± 0.1	39.3	9.8	3
$[RP(CClH_2')Ph_2]Cl$[b]	4.0[a]	30.7	5.9	6
$[RPPh_2OCH_2CH(CH_3)_2]Cl$[b]		73.1		

[a] ±0.0. [b] Peak assignments are based on literature values for the corresponding Ph_3P derivatives.[10]

The reaction is zero order in [R′OH], as is evident from the kinetic analysis and from the absence of any effect of the concentration of the alcohol on the pseudo-first-order rate constant at either 32 or 45 °C.

When the concentration of CCl_4 was changed from 6.2 to 1.55 M at 32 °C, there was no change in the pseudo-first-order rate constant (Table II). However, if the reaction is also first order in [CCl_4], the second-order rate constants $k_{obsd}/[CCl_4]$ are 0.94×10^{-4} M^{-1} s^{-1} in 6.2 M CCl_4 and 3.8×10^{-4} M^{-1} s^{-1} in 1.55 M CCl_4. The 4-fold increase in the second-order rate constant would be predicted from the increased solvating ability of the $CHCl_3$. In order to observe the order of the reaction in [CCl_4], the reaction was run at 45 °C under second-order rate conditions with 0.10 M CCl_4, 0.19 or 0.30 M 2-PEDP, and 1.0 M 2-octanol in $CHCl_3$. These data fit the rate law $d[\text{2-PEDP}]/dt = -(1.98 \pm 0.13) \times 10^{-3}$ [2-PEDP][CCl_4] M s^{-1} (correlation coefficients 0.991). The decay of the phosphines 2-PEDP and Ph_3P were also examined at 45 °C in experiments with excess CCl_4 and 2-octanol or isobutyl alcohol in $CHCl_3$. The pseudo-first-order rate constants are listed in Table II and are essentially identical, which reinforces the zero-order dependence of the reaction in alcohol. The second-order rate constant $k_{obsd}/[CCl_4]$ for the reaction of 2-octanol and 2-PEDP with 1.55 M CCl_4 is 0.91×10^{-3} M^{-1} s^{-1}, which is about half the value of the second-order rate constant obtained with 0.10 M CCl_4 and follows the trend of increasing second-order rate constant with increasing concentration of $CHCl_3$. The slow step in phosphine consumption must be the initial reaction of the phosphine with carbon tetrachloride[1,4] via paths A or B and subsequently with salt **3** or **6** (Scheme I, reactions 1–4). The reaction is 10 times faster with 2-PEDP than with Ph_3P.

When we examined the reaction of 2-PEDP with isobutyl alcohol at 45 °C, we observed the formation and decay of an isobutoxyphosphonium intermediate **2a** in the ^{31}P NMR spectrum by its signal at δ 73.1 (Tables II and III). In the experiments in which either 2:2 or 2:1 phosphine–alcohol stoichiometry was used, the intermediate was detected at approximately 300 s and reached its maximum concentration of about 0.022 M at 600 s. The intermediate was never present in high concentrations, but we were nonetheless, able to observe its buildup and subsequent decay. The isobutoxyphosphonium intermediate reached the same approximate maximum concentration in both experiments, independent of the concentration of the alcohol. The raw kinetic data were treated as though the reaction was occurring by a consecutive reaction sequence consisting of two first-order steps.[16] The product-forming step is reaction 5 in Scheme I.

$$\text{phosphine} \xrightarrow{k'} \text{RPh}_2\text{POR}'^{+}\text{Cl}^{-} \xrightarrow{k''} \text{products} \qquad (9)$$

The values for k' and k'' are 7.5×10^{-4} and 32×10^{-4} s^{-1}, respectively. Correcting k_{obsd} for the portion of phosphine that yields salts **6** and **7** and therefore would not generate intermediate **2a** (Scheme I, reactions 2 and 3), we found the total rate of formation of isobutoxyphosphonium intermediate via paths A and B should be 11×10^{-4} s^{-1}. The value of k' is about 70% of the predicted value. The half-life for the decay of **2a** (Scheme I, reaction 5) is 216 s.

We did not observe the isobutoxytriphenylphosphonium intermediate under similar conditions (Table II). Franzus et al.[13] reported the detection by ^{1}H NMR of a transient isobutoxytriphenylphosphonium intermediate that decomposed too rapidly to follow kinetically. The decomposition of **2a** is kinetically similar to the first-order decomposition of the (neopentyloxy)triphenylphosphonium intermediate **2d** studied by Weiss and Snyder[17] and Franzus et al.[12,13] In 28.6% CCl_4 in $CDCl_3$ and at ambient temperature, intermediate **2d** is reported [13] to have decomposed completely in 4.5 h.

The reactions of Ph_3P–CCl_4 with either 2-octanol or isobutyl alcohol in $CHCl_3$ yielded only salt **7b** and Ph_3PO as phosphorus-containing products. Neither salt **6b** nor the alkoxyphosphonium intermediate **2b** was observed. In excess CCl_4, the rates were independent of [ROH] and pseudo first order in [Ph_3P].

The extent of the two reaction paths was determined in the CCl_4–$CHCl_3$ mixed-solvent system by use of ^{31}P NMR as outlined in the Experimental Section (also see Table II). The calculated percentage of path A varied in each run by about 10% over each of the reaction times sampled and accounted for 40–50% of the reaction with 2-PEDP–2-octanol, 64% of the reaction with 2-PEDP–isobutyl alcohol, and 0% with Ph_3P and either alcohol. Thus, the bifunctional 2-PEDP appears to produce alkyl halide in significant amounts by both paths A and B, whereas the Ph_3P reacts almost exclusively by path B. Similarly, Tömösközi[15] reported that the reaction of alcohols and enolizable ketones with Ph_3P–CCl_4 produced considerable amounts of salts **6d** and **7d**, also indicating that path B was the major route.

The relative contributions of paths A and B have been estimated for the reactions of Ph_3P and various polymers with 1-octanol in CCl_4 solvent by measuring the number of moles of $CHCl_3$ formed and the number of moles of phosphine consumed/mol of 1-chlorooctane produced.[4] In all cases, path A accounted for only 18–29% of the 1-chlorooctane produced.

Experimental Section

General Comments. Carbon tetrachloride was purified by distillation from P_2O_5 and then stored continuously over 3-Å sieves under nitrogen. Ethanol stabilizer was removed from chloroform by shaking with concentrated H_2SO_4; the $CHCl_3$ extract was then washed with water, dried over $CaCl_2$, distilled, and stored over 3-Å sieves in a brown bottle under nitrogen. The phosphine DPP was used as obtained from Alfa. Triphenylphosphine (Aldrich) was recrystallized from cyclohexane. The alcohols 1-octanol, 2-octanol, cyclohexanol, and isobutyl alcohol were distilled before use, and purity evaluations of the alcohols and the internal standard anisole were performed by GLC and ^{1}H NMR. Neopentyl alcohol was dissolved in dichloromethane and the resultant solution dried over 3-Å sieves. The solvent was removed by rotary evaporation, and the solid alcohol was dried under vacuum for 4 h and stored under nitrogen prior to use. 1-Dodecanol and phenylacetic acid were used as obtained from Aldrich; 2-dodecanol was used directly as obtained from Lancaster Synthesis. *p*-Toluidine was treated with charcoal and recrystallized from ethanol.

GLC was carried out with a Bendix 2600 gas chromatograph (flame-ionization detector) fitted with a 7-ft column containing 10% Carbowax on Chromasorb Q as the stationary phase. Melting points (uncorrected) were determined with a Nagle hot-stage apparatus. ^{1}H NMR spectra were recorded on a Varian EM-390 spectrometer. All ^{1}H-decoupled ^{13}C NMR spectra were recorded on a General Electric QE-300 spectrometer operating at 75.48 MHz. ^{31}P NMR experiments are described below.

(Pyrid-2-ylethyl)diphenylphosphine. The method of Uhlig[18] was modified as follows: Distilled 2-vinylpyridine (8.5 g, 0.081 mol) and 0.7 mL of glacial acetic acid were added to a 50-mL round-bottom flask that was fitted with a condenser and a stir bar and purged with nitrogen. Distilled diphenylphosphine (13.0 g, 0.70 mol) was added by syringe and the mixture heated in an oil bath at 150 °C for 8 h. The crude mixture was dissolved in methanol and made basic with solid potassium carbonate. The precipitate was removed by suction filtration through Celite, and the filtrate was concentrated under vacuum. The residue was recrystallized from methanol–water at about −35 °C. The crude phosphine was chromatographed on a column of 60–230-mesh silica gel with 5% ethanol–chloroform (R_f 0.5, TLC on E. M. Merck Kieselgel 60 F_{254} plates). The yield of the purified phosphine was 61%.

Procedure for Small-Scale Chlorination Reactions. The reactions are listed in Table I. The following examples are typical.

(a) ^{1}H NMR Procedure for Monitoring Halide Formation. To an NMR tube were added 0.006 93 g (0.0514 mmol) of 2-octanol, 0.0301 g (0.104 mmol) of 2-PEDP, 0.400 mL of carbon tetrachloride, 0.275 mL of chloroform-*d* and a trace amount of tetramethylsilane as an internal reference standard. A known amount of anisole (0.005 79 g, 0.0536 mmol) was added as an internal standard for integration purposes. The probe temperature was determined prior to use with a methanol–water–hydrochloric acid calibration standard.[19] The reaction was scanned for a period of 1.5 h. The disappearance of alcohol was followed by noting the decrease in area of the $CH_3C(H)OH$ doublet at δ 1.1 and the corresponding appearance and increase in area of the $CH_3C(H)Cl$ doublet of the product at δ 1.45.

(b) Typical Gas–Liquid Phase Chromatographic Procedure. The yields from several of the reactions shown in Table I were estimated by GLC analysis. The reactions were scaled up from those outlined above by a factor of seven. A mixture of 1-octanol (0.0493 g, 0.379 mmol), 2-PEDP (0.222 g, 0.762 mmol), 0.630 mL of CCl_4, and 3.50 mL of $CHCl_3$ was stirred under nitrogen at 35 °C for 1 h. The phosphorus-containing products were extracted from the mixture by washing with 1 M HCl, followed by several water washes and subsequent drying over 3-Å sieves. There were no phosphorus-containing reaction products remaining in the organic layer. A known weight of anisole (0.0398 g, 0.368 mmol) was added as an internal standard, and the amounts of alcohol and alkyl chloride were determined by GLC analyses at 40 °C for elution of CCl_4 and $CHCl_3$ and at 110 °C for all other components.

(c) Preparation of 1-Chlorododecane. A solution of 1-dodecanol (0.222 g, 1.23 mmol), 2-PEDP (0.752 g, 2.58 mmol), 2.00 mL of CCl_4, and 12.0 mL of $CHCl_3$ was stirred at 35 °C for 1 h. The reaction mixture was washed twice each with 5.00-mL portions of 1 M HCl and with 10.0 mL of water and dried over 3-Å sieves overnight. The solution was then passed through a short silica gel column to remove any traces of phosphorus-containing reaction products, and the column was rinsed with 120 mL of

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$CHCl_3$. The bulk of the solvent was distilled off at atmospheric pressure. The residue was stirred to constant mass under N_2. The isolated product (0.259 g, 97.0%) exhibited ^1H NMR and GLC data identical with those of an authentic sample.

^{31}P NMR Data (Summarized in Tables II and III). All ^{31}P NMR spectra were run on a Nicolet NT-200 FT spectrometer operating at 80.99 MHz, with the variable-temperature 12-mm probe equilibrated at the desired temperature. All broad-band ^1H-decoupled chemical shift values are reported relative to an external 85% H_3PO_4 reference standard: positive, downfield; negative, upfield. Relevant spectral parameters were set for each run prior to the addition of the alcohol–CCl_4 mixture with a solution of the phosphine in $CDCl_3$ alone. For each ^{31}P NMR monitored kinetic run, the NMR parameters were adjusted to accommodate the compound with the longest relaxation time to ensure the collection of quantitative spectral data as outlined by Stanislawski and Van Wazer.[20] Spectra were collected by utilizing a pulse width of 18.0 μs (90° flip angle), with a delay time greater than five times the T_1 of the compound with the longest T_1 contained in the sample. In all cases, a minimum delay of 120 s was allowed between pulses. The samples were sufficiently concentrated so that spectra with good S/N were obtained with only one pulse.

(a) Spin–Lattice Relaxation Time (T_1) Studies. The experiments were run at 32 °C using a standard inversion–recovery sequence. Solvents were vacuum degassed prior to each run. The results are listed in Table III. The relaxation time of 2-PEDP was determined with a 0.15 M solution of the phosphine in $CDCl_3$. A mixture of the products of the reaction of 2-PEDP, 2-octanol, and CCl_4 (Table II, entry 2 after 1.5 h at 32 °C) was used to determine the T_1 values of the remaining compounds. Values were determined automatically by a three-parameter fit routine supplied by Nicolet for its NMC-1280 software programs.[21] $y = A[1 - [1 + W(1 - \exp(-K/T))] \exp(-x/T)]$, where A = amplitude at $x \gg T$; $T = T_1$ relaxation time(s); $K = D_2 + D_5$ in the pulse sequence; $x = D_1$ in the sequence; W = (amplitude at $x = y$) ΨA.

(b) 2-PEDP–Alcohol Reactions. To one flame-dried vial was added 2-PEDP (0.1965 g, 0.6753 mmol) dissolved in 3.82 mL of $CDCl_3$; to another was added a solution of 2-octanol (0.045 25 g, 0.3475 mmol) in 0.675 mL of CCl_4. The solutions were thermostated at 32 °C for 1 h. The phosphine–chloroform solution was then transferred to a flame-dried 12-mm NMR tube and the ^{31}P NMR spectrum checked to verify the absence of phosphine oxide contaminant in the sample prior to addition of the alcohol. The tube was then removed from the probe, and the mixture of 2-octanol and CCl_4 was added. The tube was then shaken and replaced in the probe for monitoring as described below.

(c) Ph_3P–Alcohol Reactions. Ph_3P (1.576 g, 5.999 mmol) was dissolved in 30.0 mL of a 7:8 $CHCl_3$–$CDCl_3$ mixture and thermostated at 45.0 °C. The mixture of CCl_4 (6.00 mL, 61.8 mmol) and alcohol (3.022 mmol) was added. Aliquots (4 mL) were withdrawn at appropriate intervals and frozen. The ^{31}P NMR spectra of these aliquots were obtained the following day. The following ^{31}P NMR assignments were made:[22] triphenylphosphine, δ −4.95; triphenylphosphine oxide, δ 31.1; phosphonium salt **7d** $[[(C_6H_5)_3PCClH_2]Cl]$, δ 24.9. The identity of the peak at δ 24.9 was also verified by ^{13}C NMR.[22] No signals corresponding to the phosphonium salt **6d** $[[C_6H_5)_3PCCl_2H]Cl]$[22] or to the alkoxyphosphonium salt **2d** were observed.

(d) Kinetic Analysis. The assignments were made for 2-PEDP and derivatives and are listed in Table III. As the reaction proceeded, the phosphine peak decreased in area and peaks corresponding to the phosphine oxide and phosphonium salts **6a** and **7a** appeared and continued to increase in area. The reactions were monitored until the phosphine had been consumed (<5280 s). For each spectrum taken at some time T the mole fraction of each phosphorus-containing species present was calculated by determining the ratio of each peak height relative to the sum of all the combined peak heights. The pseudo-first-order rate constants k_{obsd} were obtained by plots of ln [phosphine] vs time, which had correlation coefficients >0.99. The reaction was run at 45 °C under second-order rate conditions with 0.10 M CCl_4, 0.19 or 0.30 M 2-PEDP, and 1.0 M 2-octanol in $CHCl_3$. Values of $[CCl_4]$ were calculated by assuming that at any time the phosphine oxide concentration was equal to the concentration of the CCl_4 consumed. Treatment of the concentrations of phosphine and of CCl_4 as a mixed second-order process[16] gave linear plots with correlation coefficients of 0.991 between 15 and 70% reaction of the CCl_4.

In addition to the other phosphorus-containing species noted above, the ^{31}P NMR spectra of the reactions of 2-PEDP and isobutyl alcohol (Table III) revealed the presence of the alkoxyphosphonium chloride intermediate $[[(C_5H_4NCH_2CH_2)P(C_6H_5)_2OCH_2CH(CH_3)_2]Cl]$ **2a**, δ 73.1. The data were treated as a reaction sequence consisting of two first-order steps occurring in a series.[16] The decay of phosphine was also followed; plots of ln [2-PEDP] vs time gave good straight lines to yield values for the pseudo-first-order rate constants k_{obsd} at 45 °C.

To estimate the extent of reaction proceeding by path A, it was noted that phosphonium salts **6** and **7** are formed solely from path B, as shown in Scheme I. In the formation of 1 equiv of phosphonium salt **7** (δ 30.7), 2 equiv of phosphine oxide or intermediate **2** is produced. Correspondingly, for every 1 equiv of phosphonium salt **6** produced, an additional equiv of phosphine oxide or intermediate **2** is formed. The calculation given was performed for each data point sampled to subtract out the amount of phosphine oxide produced by path B. The percentages listed in Table II are averages over all points sampled between 13 and 90% reaction for Ph_3P and between 40 and 70% reaction for 2-PEDP.

$$N = \%\ (\text{2-PEDP oxide} + \mathbf{2})$$

$$[N - [(\%\ \text{salt } \mathbf{6}) + 2(\%\ \text{salt } \mathbf{7})]]/N \times 100 = \%\ \text{path A}$$

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