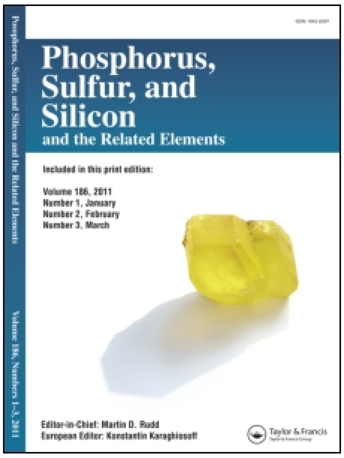

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Majewski, Piort(1998) 'Investigation of the Reaction Between Diphenylphosphine and Carbon Tetrachloride', Phosphorus, Sulfur, and Silicon and the Related Elements, 134: 1, 399 — 406

To link to this Article: DOI: 10.1080/10426509808545480

URL: http://dx.doi.org/10.1080/10426509808545480

Phosphorus, Sulfur and Silicon, 1998, Vol. 134/135, pp. 399-406
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INVESTIGATION OF THE REACTION BETWEEN DIPHENYLPHOSPHINE AND CARBON TETRACHLORIDE

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(Received 4 February, 1998)

The mechanism of diphenyltrichloromethylphosphine (**4**) formation in the title reaction has been studied. It has been established that the diphenyltrichloromethylphosphine is formed in the multistep reaction sequence (Scheme 1), which involves the intermediacy of chlorodiphenylphosphine (**2**) and tetraphenyldiphosphine (**3**). This process is analogous to the formation of dialkyltrichloromethylphosphines in the dialkylphosphine / CCl_4 reaction.

Keywords: Diphenyltrichloromethylphosphine; tetraphenyldiphosphine; chlorodiphenylphosphine

INTRODUCTION

We have recently reported on a convenient synthesis of dialkyl – and diaryl trichloromethylphosphines starting from dialkyl- or diaryl-phosphines, respectively, and carbon tetrachloride[1]. Dialkyl- and diaryltrichloromethylphosphines have been shown to undergo reversible sigmatropic rearrangement to give the reactive P-chloroylides[1b], which are starting materials for the synthesis of various phosphoroorganic compounds such as phosphonium salts, iminophosphonates, 2-chloro-alkylphosphonates and oxaphosphetanes[2–4]. Additionally the mechanism of dialkyltrichloromethylphosphine formation has been studied[5,6]. It has been found that dialkyltrichloromethylphosphines were produced via intermediacy of R_2PCl and R_2PPR_2 in a multistep reaction, in which R_2PCl plays a catalytic role[6]. We anticipated that this mechanism should be a general one for all secondary phosphines including diarylphosphines (Scheme 1).

Recently, however, it has been considered that diphenyltrichloromethylphosphine is formed in Ph_2PH/CCl_4reaction via rearrangament of the phosphonium salt intermediate (5)[7] (Scheme 2).

$$\underset{1}{Ph_2PH + CCl_4} \xrightarrow{k_1} \underset{2}{Ph_2PCl} + CHCl_3 \qquad (1)$$

$$\underset{2}{nPh_2PCl} + \underset{1}{nPh_2PH} \xrightarrow{k_2,\ nN(C_2H_5)_3} \underset{3}{nPh_2PPPh_2} + nHN(C_2H_5)_3Cl \qquad (2)$$

$$\underset{3}{nPh_2PPPh_2} + nCCl_4 \xrightarrow{k_3} \underset{4}{nPh_2PCCl_3} + \underset{2}{nPh_2PCl} \qquad (3)$$

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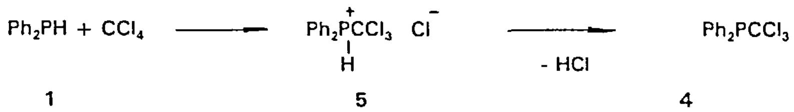
(1) + (2) + (3)

$$(n+1)Ph_2PH + (n+1)CCl_4 \xrightarrow[-n[H\overset{+}{N}(C_2H_5)_3]Cl^-]{n[(C_2H_5)_3N]} nPh_2PCCl_3 + Ph_2PCl + CHCl_3$$

SCHEME 1

In this paper we present our studies on the course of Ph_2PH/CCl_4 reaction to resolve this puzzling question about the mechanism.



$$\underset{1}{Ph_2PH + CCl_4} \longrightarrow \underset{5}{Ph_2\overset{+}{\underset{H}{P}}CCl_3\ Cl^-} \xrightarrow[-\,HCl]{} \underset{4}{Ph_2PCCl_3}$$

SCHEME 2

RESULT AND DISCUSSION

The methodology used in these studies was identical to that described when previously examining the mechanism of dialyltrichloromethylphosphine formation in the dialkylphosphine/CCl_4 reaction.[6] Influence of the proton solvent on the dialkylphosphine/CCl_4 reaction course was studied at first. Thus, when diphenylphosphine was caused to react with carbon tetrachloride in carbon tetrachloride-methanol solution (1 : 1 / v : v; 64°; 6 h) a mixture of diphenylphosphine oxide (**6**) and methyl diphenylphosphinate (**8**) in 2/1 molar ratio was produced. This points out that diphenylphosphine (**1**) is transformed into diphenylchlorophosphine (**2**), which subsequently gives rise to the formation of diphenylphosphine oxide (**6**)[8a] as well as methyl diphenylphosphinate (**8**)[8b] (Scheme 3).

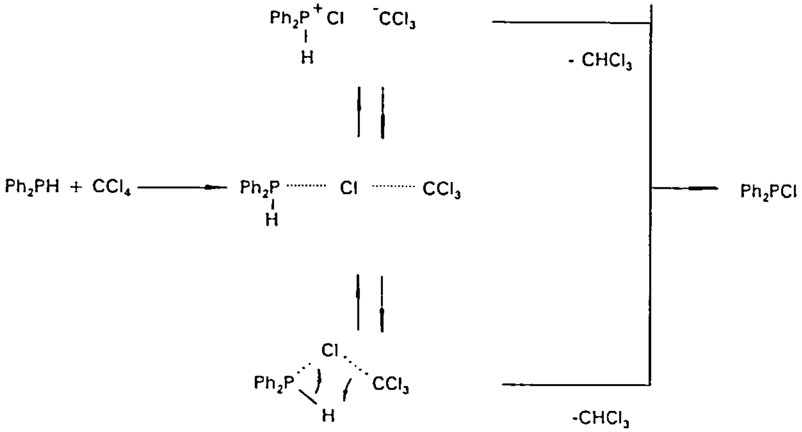
$$\underset{\mathbf{1}}{Ph_2PH} \xrightarrow[-CHCl_3]{CCl_4} \underset{\mathbf{2}}{Ph_2PCl} \xrightarrow[-CH_3Cl]{CH_3OH} \underset{\mathbf{6}}{Ph_2P(O)H} \qquad \text{(a)}$$

$$\underset{\mathbf{6}}{Ph_2P(O)H} \xrightarrow[-CHCl_3]{CCl_4} \underset{\mathbf{7}}{Ph_2P(O)Cl} \xrightarrow[-HCl]{CH_3OH} \underset{\mathbf{8}}{Ph_2P(O)OCH_3} \qquad \text{(b)}$$

SCHEME 3

It is very likely that the transformation of diphenylphosphine (**1**) into diphenylchlorophosphine (**2**) proceeds according to the Scheme 4.

The course of the title reaction has also been examined in an aprotic solvent. The reaction between diphenylphosphine (**1**) and carbon tetrachloride in the presence of triethylamine was performed at 20° and 80°, respectively and their progress was monitored by ^{31}P – NMR spectroscopy. Intermediates and end products formed in the reaction are shown in Table I.



SCHEME 4

TABLE I Molar ration distribution of intermediates and end products formed in the reaction between diphenylphosphine (**1**) and carbon tetrachloride in the presence of triethylamine in benzene solution at 20°C and 80°C, respectively *

Time (min)	*Temp. (°C)*	*Unreacted phosphine* Ph_2PH^a	*Intermediates and end products*		
			$Ph_2PPPh_2{}^b$	Ph_2PCl^c	$Ph_2PCCl_3{}^d$
5	20	100	-	-	-
	80	100	-	-	-
10	20	100	-	-	-
	80	96.6	3.4	-	-
30	20	-	-	-	-
	80	7.9	40.7	-	51.4
60	20	-	-	-	-
	80	-	-	18	82
21h	20	40	55.6	-	4.4

a) $\delta 31_p = -41.0$, lit.[8] $\delta_{31p}=-41.1$; b) $\delta_{31p}=-15.0$, lit.[8] $\delta_{31p}= -15.2$; c) $\delta_{31p}=81.2$, lit. [8] $\delta_{31p}=80.5$; d) $\delta_{31p}= 54.3$, lit.[1b] $\delta_{31p}=54.3$.

*For experminetal condition see experimental part.

The gathered data indicate that at room temperature (21h, 20°C, Table I) the diphenyldiphosphine (**3**) should also be considered as an important intermediate of the reaction.

When the reaction was carried out at elevated temperature (80°C) the maximal concentration of intermediate diphosphine was reached in about 30 minutes and then its gradual disapearing, as well as formation of the final product diphenyltrichloromethylphosphine (**4**), were observed. At the same time a small amount of chlorophosphine **2** was also produced. These observations, particularly intermediacy of Ph_2PCl as well as Ph_2PPh_2 in the title reaction, led us to conclude that Ph_2PCCl_3 was formed in the same reaction sequence (Scheme 1) in which dialkyltrichloromethylphosphine is produced in dialkylphosphine/CCl_4 reaction.[6]

We were also interested in evaluating the relative rate constants of the consecutive reaction steps in the Scheme 1. To gain insight into the reaction course we studied the influence of the Ph_2PCl on the rate of Ph_2PCCl_3 formation. It is noteworthy that chlorophosphine formed in the reaction 3 may also enter the reaction 2, being the catalyst of the transformation of Ph_2PH into Ph_2PCCl_3. The influence of the Ph_2PCl addition to the rate Ph_2PH/CCl_4 reaction is shown in Table II.

TABLE II Influence of chlorodiphenylphosphine (**2**) on the rate of the Ph_2PCl/CCl_4 reaction *

Time (min)	*Added Ph_2PCl (%)*	*Molar ration of Intermediates and end products*		
		Ph_2PPPh_2	*Ph_2PCl*	*Ph_2PCCl_3*
45	0	9.4	16.6	74.0
50	0	4.9	16.8	78.3
55	0	5.4	16.6	78.0
45	3	3.1	15.9	81.0
50	3	2.5	14.5	83.0
55	3	2.1	14.7	83.2
45	5	1.1	13.5	85.4
50	5	-	13.7	86.3
55	5	-	13.7	86.3

* For experimental conditions see experimental part.

It is seen that in the presence of 5% Ph_2PCl the reaction is complete after the time indicated in the table (50 min.). However, in other cases (0% and 3% Ph_2PCl, respectively), after the same time, formation of Ph_2PCCl_3 is also almost finished owing to a small amount of Ph_2PPPh_2 among the reaction products. It shows that Ph_2PCl has a small effect on the rate of Ph_2PCCl_3 formation. This ultimately indicates that the reactions 2 and 3 (Scheme 1) are not very fast with respect to the rate of the reaction 1 in the examined conditions. More clearcut conclusions about the rate constants can be drawn from the information that Ph_2PPh_2 appeared in large concentration during the reaction. This strongly suggests that the ratio of consecutive steps should be as follows:

$$k_1 < k_2 > k_3$$

In agreement with this conclusion is the observation that together with Ph_2PCCl_3 – a small amount of chlorodiphenylphosphine is produced.

EXPERIMENTAL

Solvents and reagent were purified by conventional methods. ^1H - and ^{31}P-NMR spectra were recorded on a DPX-Bruker Spectrometer operating at 250.13 MHz and 101.26, respectively. IR spectra were recorded on a Specord 71 IR (C. Zeiss) Spectrometer. MS spectra were recorded on a LKB-900 mass spectrometer.

Reaction of diphenylphosphine (**1**) with carbon tetrachloraide in methanol-carbon tetrachloride (1:1 /v:v) solution.

To the stirred boiling solution of carbon tetrachloride (50 mL) and methanol (50 mL) under argon, diphenylphosphine (**1**) (3.8g, 20,4 mM) was added dropwise and the mixture was kept for 6h at 64°C. Then the solvents were evaporated from the reaction mixture to afford the mixture of diphenylphosphine oxide (**6**) ($\delta^{31}P = 22.7$ ppm) and methyl diphenylphosphinate (**8**) ($\delta^{31}P = 33.1$ ppm). Molar ratio of these products based on the integrated ^{31}P-NMR, as well as ^1H-NMR signals of the crude reaction mixture was **6**/**8** = 2:1. The individual compounds have been isolated from the mixture by careful redestillation.

Diphenylphosphine oxide, b.p. 102–105°C/0,4 Torr, ^1H-NMR ($CDCl_3$) : 8.01 ppm (1H, d, J_{PH} =490Hz, PH), 7.14–7.94 ppm (m, 10H arom.), ^{31}P-NMR ($CDCl_3$): δ=22.7 ppm, lit.[9] δ=22.9 ppm, IR (P=O): 1190 cm^{-1}.

Methyl diphenylphoshinate, b.p. 140–145°C/o.4 Torr, lit.[10] b.p. 134–140°C/O.34 Torr, ^{1}H-NMR ($CDCl_3$) : 3.68 ppm (3H, d, $J_{PH} = 11$ Hz, $POCH_3$), 7.15–7.45 ppm (m, 10H arom.), ^{31}P-NMR ($CDCl_3$): δ=33.1 ppm, IR (P =O) 1240 cm^{-1}, MS (m/e, rel. int. %): 231, 232, 233 [M^+, $(M+1)^+$, $(M+2)^+$; 92, 47, 10].

Rate of formation of intermediates and diphenyltrichloromethylphosphine (**4**) in the Ph_2PH/CCl_4 reaction.

a. Reaction of diphenylphosphine (**1**) with carbon tetrachloride and triethylamine in benzene solution at 80°C.
   The benzene solution (50 mL) of carbon tetrachloride (14 mL, 22.2 g, 0.158 mol) triethylamine (0.777 g, 7.68 mM) and diphenylphosphine (**1**) (1.4 g, 7.68 mM) was stirred for 1 h under argon at reflux. During this period 10 mL samples were taken at respective time intervals, the solvent was evaporated at 0–5°C and the crude reaction mixture was analysed qualitatively and quantitatively using ^{31}P and ^{1}H-NMR measurements. The results are presented in Table I.

b. Reaction of diphenylphosphine (**1**) with carbon tetrachloride and triethylamine in methylene chloride at 20°C.
   The reaction mixture, prepared as described in experiment A (instead of benzene the methylene chloride was used), was kept under argon for 24 h at 20°C. During this period 10 mL samples were taken at respective time intervals and analysed as described above. The result are presented in Table I.

c. Reaction of diphenylphosphine (**1**) with carbon tetrachloride and triethylamine without, and in the presence of, added chlorodiphenylphosphine (**2**).
   To the reaction mixture, prepared as described in experiment A chlorodiphenylphosphine (0.0, 3.0 and 5.0 mol %, respectivly) was added and the resulting mixture was stirred for 1 h under argon at reflux. The reaction samples (10 mL), taken at respective time intervals, were analysed qualitatively and quantitatively by means of ^{31}P and ^{1}H – NMR spectroscopy. The results are presented in Table II.

Acknowledgements
The author is grateful to Professor R.Bodalski for many stimulating discussions.

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