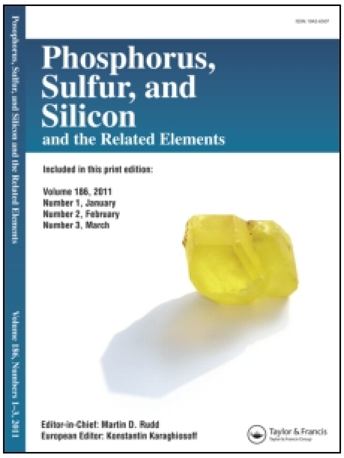

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INVESTIGATION OF THE REACTION BETWEEN DIALKYLPHOSPHINES AND CARBON TETRACHLORIDE. PART I

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INVESTIGATION OF THE REACTION BETWEEN DIALKYLPHOSPHINES AND CARBON TETRACHLORIDE. PART I

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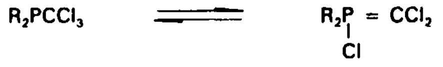
The model reaction between diethylphosphine (**3a**) and carbon tetrachloride leading to chloro(chloromethyl)diethylphosphonium chloride (**5a**) and chlorodiethylphosphine (**4a**) as the final product has been found to involve diethyltrichloromethylphosphine (**1a**) and diethylphosphine hydrogen chloride (**6a**) as the crucial intermediates. Process of the transformation of these compounds into the final products is a subject of our consideration.

Key words: Dialkyltrichlomethylphosphines; dialkylphosphines; chlorodialkylphosphines; chloro(chloromethyl)dialkylphosphonium chlorides.

INTRODUCTION

Dialkylphosphines **3** react with carbon tetrachloride forming dialkyltrichloromethylphosphines, **1**, which are useful starting materials for the synthesis of organophosphorus polymers.[1] It has been also found, that the phosphines **1** undergo reversible chlorotropic rearrangement into the corresponding P-chloroylides **2**, [2-6] (Scheme 1). Being interested in potential synthetic application of these compounds we have tried to obtain the dialkyltrichloromethylphosphines **1** using the reaction between dialkylphosphines **3** and carbon tetrachloride as described in a patent protocol.[1] However, all our attempts to reproduce this protocol, failed. For example, the model reaction between diethylphosphine (**3a**) and carbon tetrachloride led to chloro(chloromethyl)diethylphosphonium chloride (**5a**) and chlorodiethylphosphine (**4a**) instead of the expected diethyltrichloromethylphosphine (**1a**). The formation of compound **5a** having a P—C bond unequivocally implied the intermediacy of diethyltrichloromethylphosphine (**1a**) in this reaction (Scheme 2).

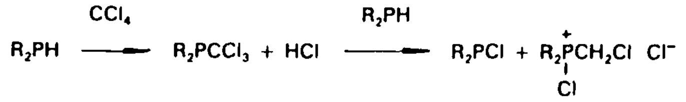
In this paper we wish to present our studies on the mechanism of the reaction between diethylphosphine (**3a**) and carbon tetrachloride. We anticipated that the conclusion resulting from these studies could be generalized and extended on analogous transformations of the relative phosphines. We also hoped that finding of a simple and effective procedure for the preparation of phosphines **1** will be possible.



$$R_2PCCl_3 \rightleftharpoons R_2\underset{\displaystyle Cl}{\underset{|}{P}}=CCl_2$$

1 **2**

Scheme 1



$$R_2PH \xrightarrow{CCl_4} R_2PCCl_3 + HCl \xrightarrow{R_2PH} R_2PCl + R_2\overset{+}{\underset{Cl}{P}}CH_2Cl\ Cl^-$$

3 **1** **4** **5**

1, 3, 4, 5	R
a	C_2H_5

Scheme 2

RESULT AND DISCUSSION

Intermediates and Final Products in the Reaction between Diethylphosphine (**3a**) *and Carbon Tetrachloride*

The model reaction between diethylphosphine (**3a**) and carbon tetrachloride was performed at room temperature and its progress was monitored by ^{31}P-NMR spectroscopy. This technique allows differentiating two subsequent stages of the reaction.

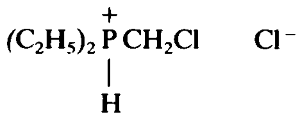
In the first stage the appearance of the intermediate having a signal of $\delta_{^{31}P}$ = 58.0 ppm was observed. At the same time the signal of the starting phosphine with $\delta_{^{31}P}$ = −55.0 ppm was gradually shifted downfield achieving the value of $\delta_{^{31}P}$ = −17.0 ppm, characteristic for the second intermediate.

In the second stage the signals of both intermediates formed in the first stage were gradually decreasing and the signal of $\delta_{^{31}P}$ = −17.0 ppm was disappearing faster. The disappearance of the initial intermediates resulted in the appearance of the new secondary intermediates of $\delta_{^{31}P}$ (ppm): 15.2; 19.0; 54.2; 59.0 and 75.8. The final products were not produced at the same time. Chlorophosphine **4a** ($\delta_{^{31}P}$ = 118.0 ppm, lit.[7] $\delta_{^{31}P}$ = 119.9 ppm) was formed at the beginning, and chloro(chloromethyl)diethylphosphonium chloride (**5a**) ($\delta_{^{31}P}$ = 104.3 ppm) at the end of the second reaction stage. These compounds were isolated and their structure was unambiguously assigned using ^{1}H-NMR spectroscopy.

The products formed in the first reaction stage have been also carefully examined. The MS spectrum of the reaction mixture shown that its phosphoroorganic component of $\delta_{^{31}P}$ = 58.0 ppm is diethyltrichloromethylphosphine (**3a**) (MS as well as its ^{31}P-NMR chemical shift was identical with that reported for diethyltrichloromethylphosphine[2]). The second intermediate of $\delta_{^{31}P}$ = −17.0 ppm was proved to be diethylphosphine hydrogen chloride (**6a**). It has been isolated from the reaction mixture and its identity was confirmed by its spectral (^{1}H- and ^{31}P-NMR) and analytical data, as well as by the neutralization to the free phosphine **3a**.

Attempts to characterize intermediates which are formed in the second reaction stage led to the separation of (chloromethyl)diethylphosphine hydrogen chloride

(**7a**) ($\delta_{^{31}P}$ = 19.0 ppm), whose structure was fully confirmed by ^{31}P- and ^{1}H-NMR spectroscopy.



$$(C_2H_5)_2\overset{+}{\underset{\mid\atop H}{P}}CH_2Cl \quad Cl^-$$

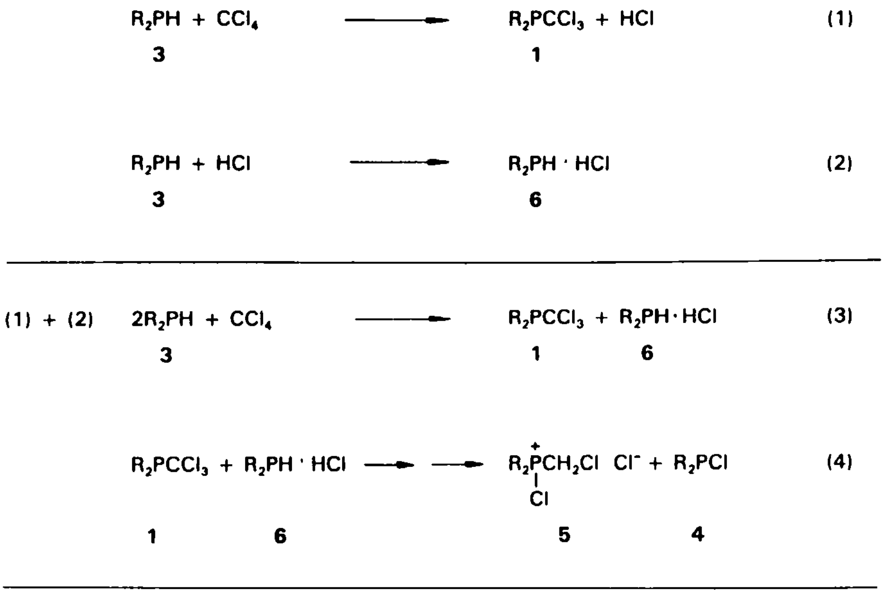
7a

General Remarks on the Course of the Title Reaction

In the light of the presented findings it is obvious that the first stage of the reaction between the phosphine **3a** and carbon tetrachloride leads to the formation of diethyltrichloromethylphosphine (**1a**) as well as diethylphosphine hydrogen chloride (**6a**) (Scheme 3, reaction 1 and 2, respectively). The chloride **6a** is produced by protonation of the unreacted starting phosphine by hydrogen chloride being a by-product in the reaction 1. The observed shift of the diethylphosphine (**3a**) signal at $\delta_{^{31}P} = -55.0$ ppm to the value of $\delta_{^{31}P} = -17.0$ ppm characteristic for diethylphosphine hydrogen chloride (**6a**) calls for the dynamic equilibrium between **3a** and **6a**. The position of this signal depends on the molar ratio of **3a** and **6a**.

The second stage of the reaction in which diethyltrichloromethylphosphine (**1a**) reacts with diethylphosphine hydrogen chloride (**6a**) to afford chlorodiethylphosphine (**4a**) and chloro(chloromethyl)diethylphosphonium chloride (**5a**) (Scheme 3, reaction **4**) seems to be a very complex process with a large number of intermediates including also (chloromethyl)diethylphosphine hydrogen chloride (**7a**).

The mechanistic pathway for the reaction of the phosphine **3** with carbon tetrachloride can be depicted as follows:



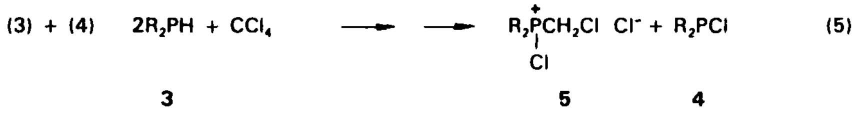
$$\underset{\mathbf{3}}{R_2PH} + CCl_4 \longrightarrow \underset{\mathbf{1}}{R_2PCCl_3} + HCl \qquad (1)$$

$$\underset{\mathbf{3}}{R_2PH} + HCl \longrightarrow \underset{\mathbf{6}}{R_2PH \cdot HCl} \qquad (2)$$

$$(1) + (2) \quad \underset{\mathbf{3}}{2R_2PH} + CCl_4 \longrightarrow \underset{\mathbf{1}}{R_2PCCl_3} + \underset{\mathbf{6}}{R_2PH \cdot HCl} \qquad (3)$$

$$\underset{\mathbf{1}}{R_2PCCl_3} + \underset{\mathbf{6}}{R_2PH \cdot HCl} \longrightarrow \longrightarrow \underset{\mathbf{5}}{R_2\overset{+}{\underset{\mid\atop Cl}{P}}CH_2Cl\ Cl^-} + \underset{\mathbf{4}}{R_2PCl} \qquad (4)$$

Scheme 3



$$(3) + (4) \quad 2R_2PH + CCl_4 \longrightarrow \longrightarrow R_2\underset{Cl}{\overset{+}{P}}CH_2Cl\ Cl^- + R_2PCl \quad (5)$$

1, 3, 4, 5, 6	R
a	C_2H_5

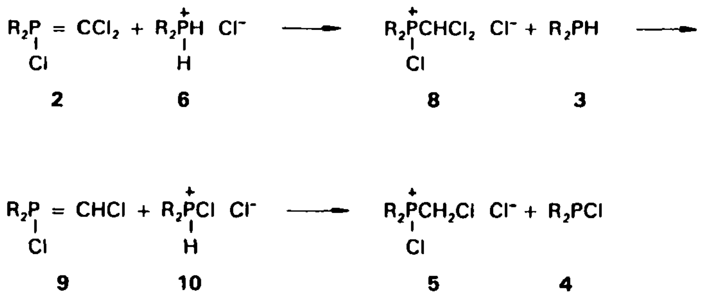
Scheme 3 (*Fortsetzung*)

Preliminary recognition of the dialkylphosphine-carbon tetrachloride reaction lead us to find a convenient and useful approach to the synthesis of dialkyltrichloromethylphosphines **1**. It has been found that the phosphines **1** are formed in high yield if the reaction is performed in an aprotic solvent and in the presence of triethylamine at low temperature.[2] Under these conditions dialkylphosphine, **3**, does not react with hydrogen chloride to form the reactive chloride **6** but exclusively undergoes the desirable reaction.

Some aspects of the formation of dialkyltrichloromethylphosphine **1** as well as the transformation of phosphine **3** and phosphine hydrogen chloride **6** into chlorodialkylphosphine **4** and chloro(chloromethyl)dialkylphosphonium chloride **5** seem to be worthy of elucidation. The latter process is a subject of our further considerations.

Transformation of Dialkyltrichloromethylphosphine 1 *and Dialkylphosphine Hydrogen Chloride* 6 *into Chlorodialkylphosphine* 4 *and Chloro(chloromethyl)dialkylphosphonium Chloride* 5

Two mechanistic pathways can be considered for the title transformation. One of them (Scheme 4) might involve the reaction of P-chloroylide **2** with dialkylphos-



$$\underset{\mathbf{2}}{R_2\underset{Cl}{P}=CCl_2} + \underset{\mathbf{6}}{R_2\underset{H}{\overset{+}{P}}H\ Cl^-} \longrightarrow \underset{\mathbf{8}}{R_2\underset{Cl}{\overset{+}{P}}CHCl_2\ Cl^-} + \underset{\mathbf{3}}{R_2PH} \longrightarrow$$

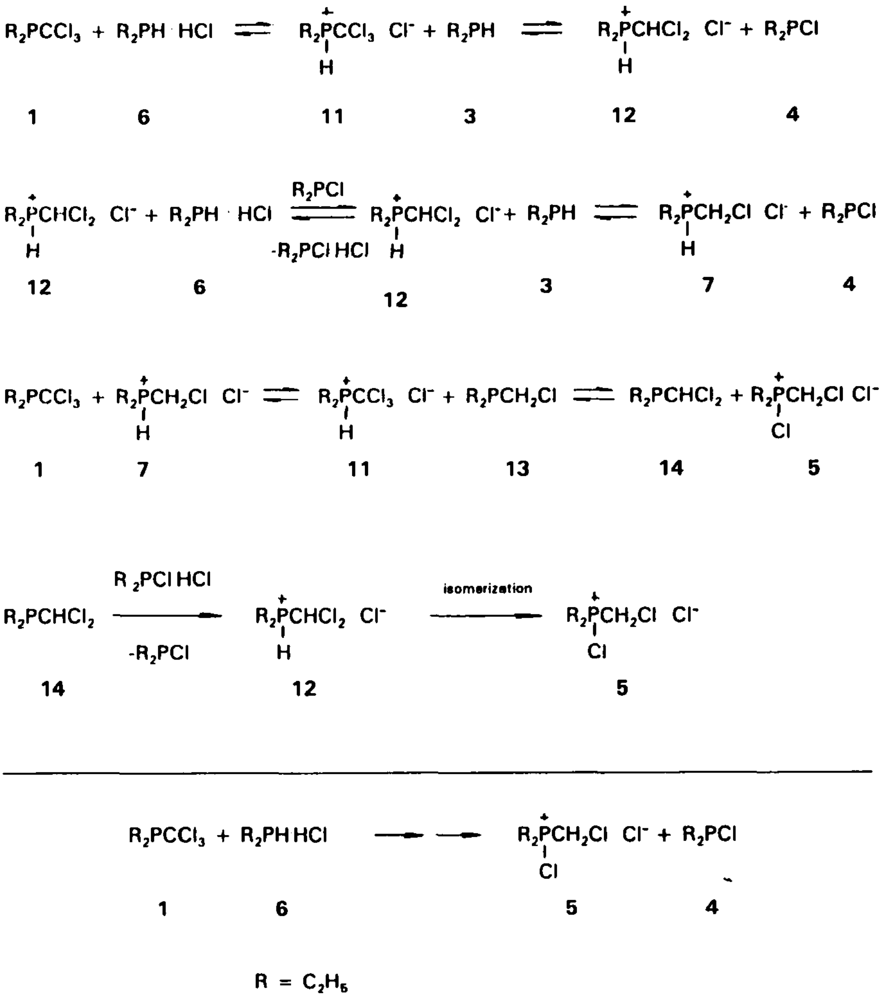
$$\underset{\mathbf{9}}{R_2\underset{Cl}{P}=CHCl} + \underset{\mathbf{10}}{R_2\underset{H}{\overset{+}{P}}Cl\ Cl^-} \longrightarrow \underset{\mathbf{5}}{R_2\underset{Cl}{\overset{+}{P}}CH_2Cl\ Cl^-} + \underset{\mathbf{4}}{R_2PCl}$$

$R = C_2H_5$

Scheme 4

phine hydrogen chloride **6** producing chloro(chloromethyl)dialkylphosphonium chloride **8** and dialkylphosphine **3** which in turn would react further giving rise to the formation of the final products, chlorophosphine **4** and chlorophosphonium chloride **5**.

The second mechanism would follow a multistep reaction sequence (Scheme 5). The first step would involve proton exchange between the phosphine hydrogen chloride, **6**, and the phosphine **1**, giving the phosphine hydrogen chloride **11** and the phosphine **3**. The attack of the phosphine **3** on the chlorine atom of the trichloromethyl group of **11** would produce the chloride **12** and the chlorophosphine **4**. Further steps are analogous to the first one involving the reactions between phosphines and phosphine hydrogen chlorides containing—CCl_3, —$CHCl_2$ and —CH_2Cl groups—which mostly rely on a hydrogen exchange and subsequent dehalogenation.



Scheme 5

It has been already shown that the discussed transformation represents a multistep complex process with a large number of intermediates among them (chloromethyl)diethylphosphine hydrogen chloride (**7a**) was found. These findings imply that the transformation may undergo according to Scheme 5.

Further support for such a mechanism was also obtained from the studies on the reaction between chloro(dichloromethyl)diethylphosphonium chloride (**8a**) and diethylphosphine (**3a**), which formally may be treated as a crucial step in the alternative mechanistic pathway (Scheme 4). It has been found that this model reaction was rapid (at temperature −50°C– +20°C, 25 min) and resulted in the formation of the expected chlorophosphine **4a** and chlorophosphonium chloride **5a** in ratio of 1:1. This indicates that if the discussed transformation occurred according to Scheme 4, ^{31}P-NMR monitoring would not reveal any intermediate but only formation of the final products in equimolar ratio. This finding may be considered as an indirect evidence that the discussed transformation proceeds according to Scheme 5.

EXPERIMENTAL

^{1}H-NMR spectra were measured at 80 MHz with a Tesla BS 487 C spectrometer. ^{31}P-NMR spectra were measured at 36.43 MHz with a Bruker HFX 90 spectrometer. Solvents and reagents were purified by conventional methods.

Reaction between diethylphosphine (**3a**) *and carbon tetrachloride.*

Carbon tetrachloride (7.69 g, 0.05 mol) was added dropwise with stirring to a solution of diethylphosphine (**3a**) (4.5 g, 0.05 mol) in chloroform (20 ml) at 20°C. Stirring was continued for 1 h at 20°C and then the mixture was kept at 20°C for 24 h. During this period samples were taken at different time intervals for qualitative and quantitative analysis of products using ^{31}P-NMR spectroscopy. The results are presented in "Results and Discussion."

—After 1 h a sample of the reaction mixture (0.01 mol of P-compounds based on starting diethylphosphine) was diluted with ether (25 ml).

The separated oil was collected and kept under reduced pressure (20_{Torr}, 15 min, 30°C) to yield diethylphosphine hydrogen chloride (**6a**); yield: 0.57 g (91%), syrupy oil. ^{31}P-NMR (CH_2Cl_2): $\delta = 17.0$ ppm. ^{1}H-NMR (CH_2CL_2): $\delta = 1.13$ (6H, dt, $^3J_{PH} = 21$ Hz, $^2J_{HH} = 7.5$ Hz, CH_3), 2.2 (4H, dq, $^2J_{PH} = 14$ Hz, $^3J_{HH} = 7.5$ Hz, CH_2), 8.1 (2H, s, PH). The neutralization of **6a** with triethylamine gave quantitatively diethylphosphine (**3a**): ^{31}P-NMR: $\delta = -55.0$ ppm, lit.[7] ^{31}P-NMR: $\delta = 55.5$.

The remaining solution contained diethyltrichloromethylphosphine (**1a**); yield: 0.88 g (85%, based upon methanolysis into dichloromethyldiethylphosphine oxide[2]). ^{31}P-NMR: $\delta = 58.0$ ppm, lit.[2] ^{31}P-NMR: $\delta = 58.0$ ppm. MS spectrum was identical with that of an authentic sample.[2]

—After 2 h a sample of the reaction mixture (0.02 mol of P-compounds based on starting diethylphosphine) was diluted with benzene (25 ml), partly evaporated at 20°C under reduced pressure and cooled (5°C, 0.5 h). The separated oil was isolated and kept under reduced pressure (20_{Torr}, 5 min, 20°C) to give chloromethyldiethylphosphine hydrogen chloride (**7a**); yield 0.22 g (6.3%), oil. ^{31}P-NMR(CH_2Cl_2): $\delta = 19.0$ ppm. ^{1}H-NMR (CD_2Cl_2): $\delta = 1.35$ ppm (6H, dt, $^3J_{PH} = 21$ Hz, $^3J_{HH} = 8$ Hz, $CH_2C\underline{H}_3$), 2.6 ppm (4H, m, $^2J_{PH} = 16$ Hz, $^3J_{HH} = 8$ Hz, $C\underline{H}_2CH_3$), 4.75 ppm (2H, d, $^2J_{PH} = 7.5$ Hz, $CH_2\overline{Cl}$), 9.5 ppm (1H, s, PH). Microanalysis of **7a** has not been performed due to its inefficient stability.

—After 24 h the reacting mixture (0.02 mol of P-compounds based on starting phosphine) was evaporated (25_{Torr}, 15 min, 25°C) and the residue was treated with ethyl ether (25 ml).

The precipitated chloro(chloromethyl) diethylphosphonium chloride (**5a**) was filtered off and recrystalized (methylene chloride-ethyl ether); yield: 1.78 g (85%), m.p. 186–188°C. ^{31}P-NMR (CH_2Cl_2): $\delta = 104.3$ ppm. ^{1}H-NMR ($CDCl_3$): $\delta = 1.45$ ppm (6H, dt, $^3J_{PH} = 23.5$ Hz, $^3J_{HH} = 7.5$ Hz, $CH_2C\underline{H}_3$), 3.3 ppm (4H, dq, $^2J_{PH} = 9.5$ Hz, $^3J_{HH} = 7.5$ Hz, $C\underline{H}_2CH_3$), 5.5 ppm (2H, d, $^2J_{PH} = 3.2$ Hz, $CH_2\overline{Cl}$).

Anal. $C_5H_{12}Cl_3P$	Calc.	C 28.66	H 5.77	P 14.79
(209.5)	Found	28.35	5.75	14.60

The etheral filtrate was evaporated to leave chlorodiethylphosphine (**4a**); yield: 1.08 g (87%), b.p. 129–130°C, lit.[8] b.p. 131–132°C. ^{31}P-NMR($CHCl_3$): δ = 118.0 ppm. lit.[7] ^{31}P-NMR: δ = 119.0 ppm.

Synthesis of chloro(dichloromethyl)diethylphosphonium chloride (**8a**).

Dichloromethyldiethylphosphine oxide[9] (1.89 g, 0.01 mol) dissolved in methylene chloride (5 ml) is added dropwise to a stirred solution of phosgene (0.99 g, 0.01 mol) in methylene chloride (10 ml) at 20°C and the mixture is set aside for 12 h at room temperature. The resulting mixture is evaporated and the residue crystallized (methylene chloride-ethyl ether) to afford phosphonium chloride **8a**; yield 1.97 g (78.5%), m.p. 144–146°C, lit.[2] m.p. 144–146°C. ^{31}P-NMR (CH^2Cl_2): 85.0 ppm. ^{1}H-NMR (CH_2Cl_2): 1.31 ppm (6H, dt, $^3J_{PH}$ = 24 Hz, $^3J_{HH}$ = 7.5 Hz, CH_3), 3.25 ppm (4H, dq, $^2J_{PH}$ = 10 Hz, $^2J_{PH}$ = 7.5 Hz, CH_2), 8.8 ppm (1H, d, $^2J_{PH}$ = 10 Hz, $CHCl_2$).

Reaction between chloro(dichloromethyl)diethylphosphonium chloride (**8a**) *and diethyl-phosphine* (**3a**).

The solution of diethylphosphine (**3a**) (0.9 g, 0.01 mol) in methylene chloride (15 ml) was added dropwise with stirring to a solution of phosphonium chloride (**8a**) (2.44 g, 0.01 mol) in methylene chloride (15 ml) at −50°C under dry argon and the resulting mixture was kept at room temperature for 15 min. Then the mixture was evaporated and to the residue dry ethyl ether was added (15 ml).

The precipitated chloro(chloromethyl)diethylphosphonium chloride (**5a**) was filtered off and recrystallized (methylene chloride-ethyl ether); yield 0.89 g (85%), m.p. 186–188°C. Spectroscopic properties of **5a** were identical with that given for **5a** isolated from the reaction between phosphine **3a** and carbon tetrachloride.

After evaporation of the filtrate, the residue was distilled to give chlorodiethylphosphine (**4a**); yield 0.49 g (0.79%), b.p. 129–130°C.

ACKNOWLEDGEMENTS

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