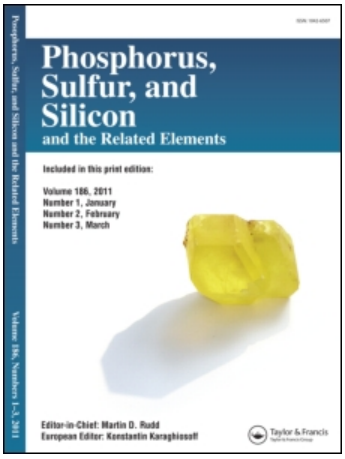

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INVESTIGATION OF THE REACTION BETWEEN DIALKYLPHOSPHINES AND CARBON TETRACHLORIDE. PART II

Piotr Majewski[a]
[a] Institute of Organic Chemistry, Technical University, Łodź, Poland

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

PIOTR MAJEWSKI

Institute of Organic Chemistry, Technical University, Żwirki 36, 90-924 Łodź, Poland

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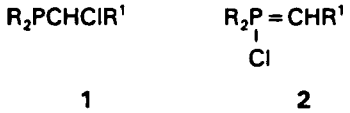
Mechanism of the formation of diethyltrichloromethylphosphine (**3a**) in the model reaction between diethylphosphine (**5a**) and carbon tetrachloride in the presence of triethylamine has been studied. It has been found that chlorodiethylphosphine (**6a**) increases the rate of the formation of the phosphine **3a**, whereas methanol changed the reaction course to produce diethylphosphine oxide (**13a**) as a major product. This findings let us to propose that the transformation of diethylphosphine (**5a**) into diethyltrichloromethylphosphine (**3a**) involves the multistep reaction sequence (Scheme 8) which includes the formation of chlorodiethylphosphine (**6a**) and tetraethyldiphosphine (**18a**) as the crucial intermediates.

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

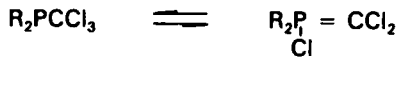
INTRODUCTION

The access to the 1-halogenoalkylphosphines **1**, as well as their reversible chlorotropic rearrangement to the reactive P-chloroylides **2**, has provided the opportunities to prepare various valuable phosphoroorganic products and intermediates such as phosphonium salt, iminophosphonates, 2-chloroalkylphosphonates and oxaphosphonates.[1–4]



1 **2**

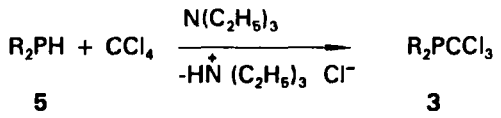
We have recently reported on a convenient preparation and on synthetic utility of the dialkyltrichloromethylphosphines, **3**.[5,6] Additionally, we have demonstrated that these compounds are also involved in the reversible chlorotropic rearrangement providing the corresponding P-chloroylides, **4**, (Scheme 1). The phosphines **3** are prepared by treatment of dialkylphosphines **5** with carbon tetrachloride in the



3 **4**

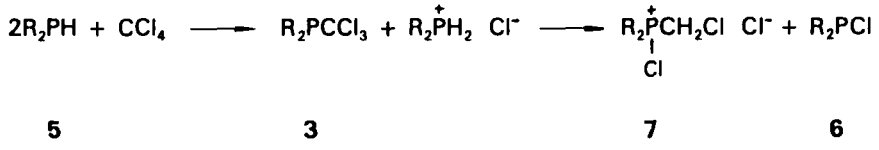
R = alkyl

Scheme 1



R = alkyl

Scheme 2



R = alkyl

Scheme 3

presence of triethylamine in an aprotic solvent.[5] (Scheme 2). This reaction performed in the absence of triethylamine leads to dialkylchlorophosphines, **6**, and chloro(chloromethyl)dialkylphosphonium chlorides, **7**, via phosphines, **3**, as intermediates (Scheme 3). The way of the transformation of the phosphine **5** into the final products **6** and **7** has been recognized,[7] however, the process of the formation of the dialkiltrichloromethylphosphine **3** has not been examined yet.

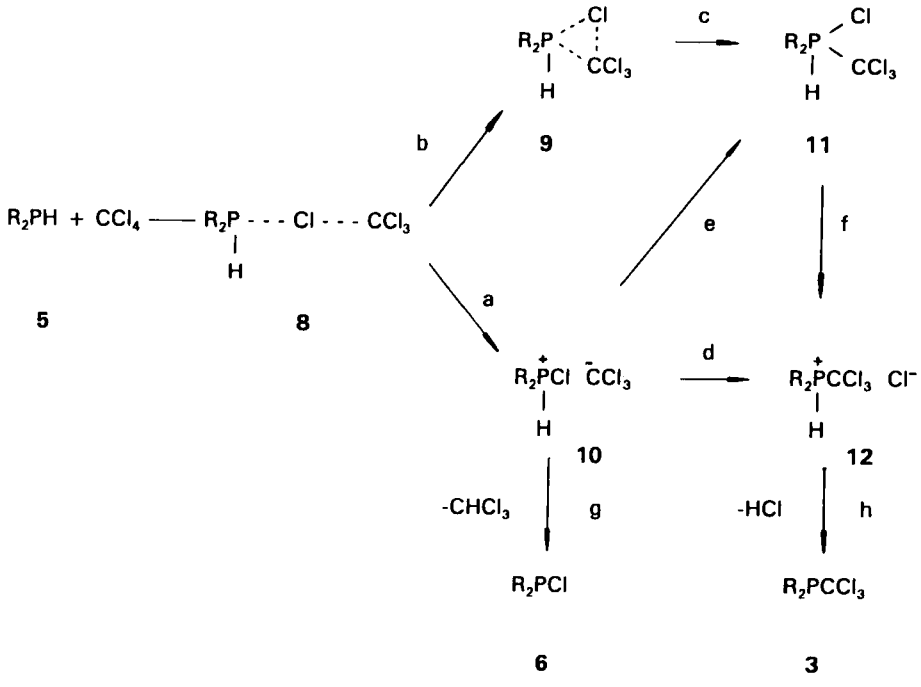
In this paper the influence of a protic solvent on the course of the model reaction between diethylphosphine (**5a**), carbon tetrachloride and triethylamine has been studied. As might be expected the change of an aprotic for a protic solvent should result in different reaction products owing to the potential susceptibility of the respective intermediates for solvolysis. Additionally kinetics of the model reaction producing diethyltrichloromethylphosphine (**3a**), catalyzed by diethylchlorophosphine (**6a**) in methylene chloride as an aprotic solvent has also been investigated. On the basis of our findings we discuss the mechanism of the formation of diethyltrichloromethylphosphine (**3a**).

RESULT AND DISCUSSION

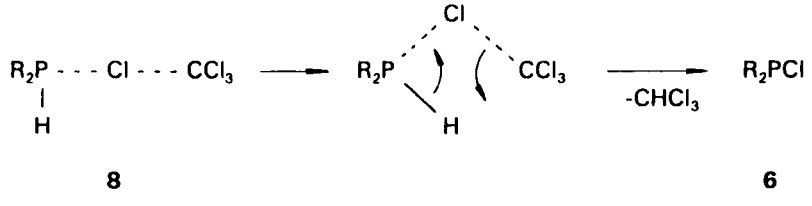
The Working Mechanistic Hypothesis

The formation of phosphine **3** is a puzzling question because none of the known pathways leading to the P—C bond does describe this process satisfactorily. It should not be the S_N2 reaction, as it may appear at the first sight, because tricoordinate phosphorus compounds react with carbon tetrachloride to form compounds containing a P—Cl bond as the primary products or the intermediates.[8-13]

If the reaction between diethylphosphine **5** and carbon tetrachloride proceeded in a similar way as the R_3P—CCl_4 reaction,[14] the phosphine **3** should be formed via intermediacy of the dipolar associate **8** by the pathways b, c, f, h or a, d, h (Scheme 4).



Scheme 4



Scheme 5

The pathway a, d, h, can be definitively rejected if one considers the potential properties of intermediate **10**. It is obvious because the phosphonium cation of the intermediate **10** should be easily deprotonated by the strongly basic trichloromethyl anion yielding chlorophosphine **6**.

The pathway b, c, f, h (Mechanism A) might also not be the real mechanism for the formation of the phosphine **3**. The strongly electronoaccepting character of the trichloromethyl moiety as well as high acidity of the hydrogen connected with the phosphorus atom of the dipolar associate **8** let us to suppose that this intermediate should rather rearrange to give the chlorophosphine **6** (Scheme 5) than the phosphine **3**. However, since the above prediction is not consistent with the experimental observation—the phosphine **3** and not the chlorophosphine **6** is formed—the pathway b, c, f, h can not be excluded.

We must take also into account that the formation of the phosphine **3** may involve a mechanism quite different from that reminiscent to the R_3P/CCl_4 reaction.[14a] It

TABLE I

Products formed in the reaction between diethylphosphine (**5a**), carbon tetrachloride and triethylamine in methylene chloride-methanol (2:1/v:v) at 20°C

Product	Molar ratio (%)	b.p. (°C)/Torr or m.p. (°C)	^{31}P-NMR δ(ppm)	^{1}H-NMR δ(ppm), J(Hz)
$(C_2H_5)_2P(O)H$ **13a**	46	54–55/0.5 lit.[19] 53–54/0.5	38.6 lit.[19] 37.0	6.64 (1H, m, $^{1}J_{PH}$ = 447, $^{3}J_{HH}$ = 3.5, PH)
$(C_2H_5)_2P(O)OCH_3$ **14a**	50	87/12 lit.[20] 86/12	60.7	3.67 (3H, d, $^{3}J_{PH}$ = 11, $POCH_3$)
$(C_2H_5)_2P(O)CHCl_2$ **15a**	4	47–48 lit.[21] 47–48	55.2 lit.[21] 55.2	5.95 (1H, d, $^{2}J_{PH}$ = 1.4, $CHCl_2$)

is possible that the dipolar associate **8** is transformed, to a small extent, into chlorophosphine **6** [via path a, g (Scheme 4) or by the rearrangement according to Scheme 5] and this process is followed by the fast formation of the phosphine **3** via chlorophosphine **6** as an intermediate (Mechanism B), vide infra.

Influence of a Protic Solvent on the Course of the Model Reaction

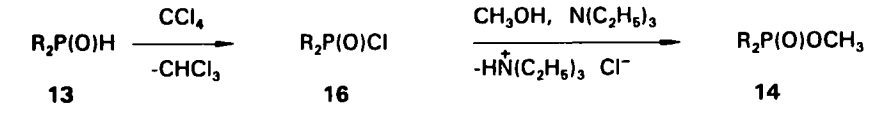
In order to gain a better understanding of dialkyltrichloromethylphosphine **3** formation the effect of a protic solvent on the course of the model reaction has been examined. This methodology is very often used in mechanistic studies to get information on the existence as well as the nature of the intermediates.[14b,15–18]

Thus, when the phosphine **19a** was treated with equimolar amount of carbon tetrachloride and triethylamine in methylene chloride-methanol solution (1:2/v:v; 20°C, 24 h) a mixture of three phosphoroorganic compounds was produced. These compounds were cleanly separated by flash chromatography and subsequently analyzed using IR, ^{31}P-NMR and ^{1}H-NMR spectroscopy.

On the basis of the obtained data their structures were identified as diethylphosphine oxide (**13a**), methyl diethylphosphinate (**14a**) and dichloromethyldiethylphosphine oxide (**15a**). Physical constants and spectroscopic data of **13a**, **14a**, **15a** as well as their molar contents in the crude reaction mixture are given in Table I.

There is no doubt that under the reaction condition diethylphosphine oxide is partly converted into the methyl phosphinate **14**[21,22a] (Scheme 6).

This finding and the date presented in Table I reveal that about 96% of the phosphine **5a** is transformed to the phosphine oxide **13a**.



13, 14, 16 **a**
R C_2H_5

Scheme 6

The dipolar associate **8** or/and chlorophosphine **6** might be considered as the potential intermediates of the phosphine oxide **13** (Scheme 7).

Chlorophosphines are known to undergo methanolyses very easily. In turn, the assumption that the dipolar associate **8** reacts with methanol is in agreement with the observation that the dipolar associate **17**, formed in the $(C_6H_5)_3P—CCl_4$ reaction, is very easily trapped by a protic solvent.[23,24]

$$(C_6H_5)_3P\cdots\cdots Cl\cdots\cdots CCl_3$$

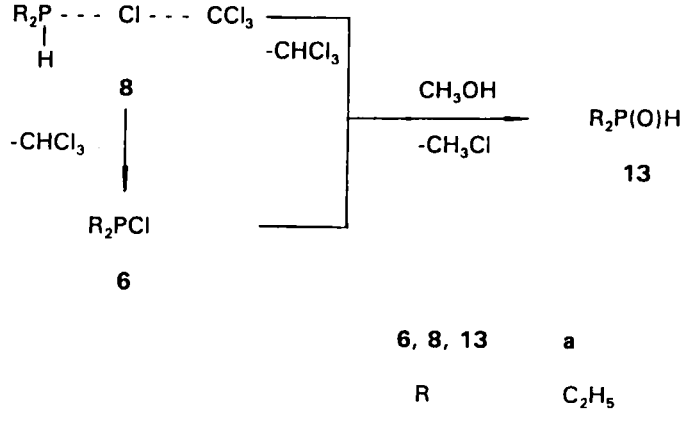
The dipolar associate **8** and/or chlorophosphine **6** seem to be also the crucial intermediates when the model reaction is carried out in an aprotic solvent affording the phosphine **3**. It is noteworthy that this conclusion is consistent with the earlier discussed mechanistic thesis (Mechanism A and B) on the formation of the phosphine **3**.

The formation of dichloromethyldiethylphosphine oxide (**15a**), 4% (Table I), implies that even in the protic solvent a small amount of the phosphine **5** reacts with carbon tetrachloride affording diethyltrichloromethylphosphine (**3a**) which is in situ methanolized to give the phosphine oxide **15**.

It is likely that under these conditions the phosphine **3** is formed via S_N2 reaction, involving nucleophilic attack of the diethylphosphine (**5a**) on the carbon atom of carbon tetrachloride to afford directly the phosphine hydrogen chloride **12**.

The formation of the phosphine **3** in a methanolic solution may also be considered in terms of the mechanism A. This might be the case if the examined reaction would proceed exclusively via the dipolar associate rearrangement. In that situation the small amount of the dipolar associate **8a** might not be trapped by protic solvent giving rise to the formation of the phosphine **3a**. This reaction course is similar to that involving the $(C_6H_5)_3P—CCl_4$ reaction in which only a part of the dipolar associate **17** reacts with a protic solvent.[14b]

From these consideration follows that the transformation diethylphosphine-diethyltrichloromethylphosphine may proceed in mechanistically inhomogeneous fashion, in which phosphine **3a** is formed partly via Mechanism B (major fraction)



Scheme 7

and partly via Mechanism S_N2 (minor fraction) or in mechanistically homogeneous manner via the pathway b, c, f, h (Scheme 4, Mechanism A).

*Influence of Chlorodiethylphosphine (**6a**) Upon the Rate of the Model Reaction*

In order to determine which of these two mechanistic possibilities is really operating we studied the influence of the addition of chlorodiethylphosphine (**6a**) upon the rate of the model reaction in methylene chloride. We expected that such an additive might effect the reaction rate when the formation of the phosphine **3a** proceeds by the Mechanism B. However, if the phosphine **3a** had been formed according to the path b, c, f, h (Scheme 4, Mechanism A) the rate of its formation would have not been changed. Attempts to accelerate the model reaction using chlorophosphine **6a** were successful. The result are shown in Figure 1.

It can be seen that the reaction rate increases with the increasing concentration of chlorophosphine **6a**. This result excludes the Mechanism A and indicates that the formation of the phosphine **3a** proceeds via chlorophosphine **6a** as an intermediate (Mechanism B). The formation of the phosphine **3a** can be fully described according to the Scheme 8.

The first step involves the reaction of the diethylphosphine (**5a**) with carbon tetrachloride to form chlorophosphine **6a** (reaction 1). Then **6a** reacts with the starting phosphine **5a** affording diphosphine **18a** (reaction 2), which in turn reacts further with carbon tetrachloride to produce chlorophosphine **6a** and diethyltrichloromethylphosphine (**3a**). It should be emphasized that the chlorophosphine

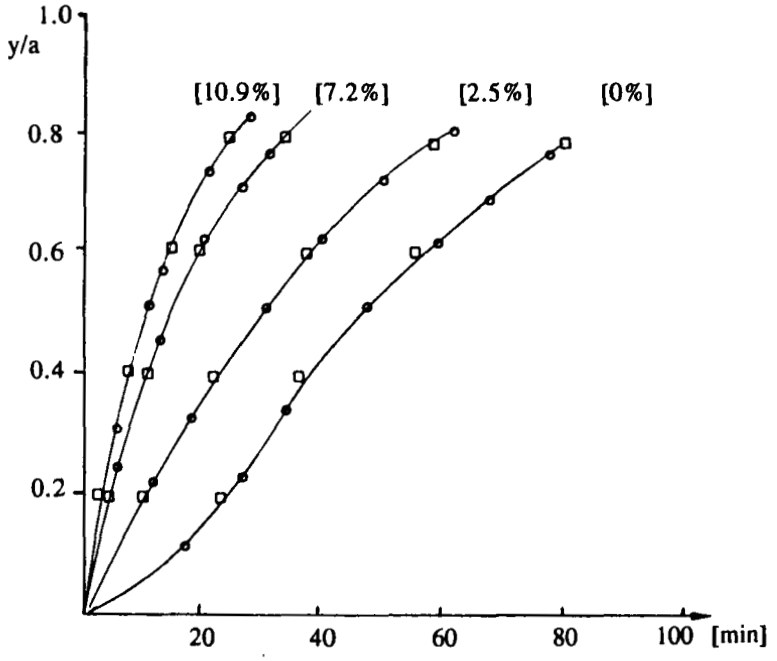


FIGURE 1 The experimental ○ and the calculated □ time dependent molar ratio of diethyltrichloromethylphosphine/diethylphosphine, y/a, for individual concentrations of used chlorophosphine. The molar percent of added chlorophosphine is given in brackets.

$$\underset{\mathbf{5}}{R_2PH} + CCl_4 \xrightarrow{k_1} \underset{\mathbf{6}}{R_2PCl} + CHCl_3 \qquad (1)$$

$$n\underset{\mathbf{6}}{R_2PCl} + n\underset{\mathbf{5}}{R_2PH} \xrightarrow[-n\,[\overset{+}{H}N(C_2H_5)_3\ Cl^-]]{n\,[(C_2H_5)_3N],\ k_2} \underset{\mathbf{18}}{nR_2PPR_2} \qquad (2)$$

$$\underset{\mathbf{18}}{nR_2PPR_2} + nCCl_4 \xrightarrow{k_3} \underset{\mathbf{3}}{nR_2PCCl_3} + \underset{\mathbf{6}}{nR_2PCl} \qquad (3)$$

---

(1) + (2) + (3)

$$(n+1)\underset{\mathbf{5}}{R_2PH} + (n+1)CCl_4 \xrightarrow[-n[\overset{+}{H}N(C_2H_5)_3\ Cl^-]]{n[(C_2H_5)_3N]} \underset{\mathbf{3}}{nR_2PCCl_3} + \underset{\mathbf{6}}{R_2PCl} + CHCl_3 \qquad (4)$$

3, 5, 6, 18	**a**
R	C_2H_5

Scheme 8

being formed in the reaction **3** also enters the reaction **2** playing a role of catalyst in the overall reaction.

To rationalize the formation of the phosphine **3a** one has to assume that the reactions 2 and 3 are very fast with respect to the rate of the reaction 1.

$$k_1 \ll k_2 \sim k_3 \qquad (1)$$

It is noteworthy that each of the reaction in Scheme 8 is known and described in details.[22b,25-28]

An essential support for this mechanistic picture is provided by the kinetic study on the formation of phosphine **3a**. From the data shown in Figure 1 unambiguously results that the reaction rate measured experimentally is consistent with that which is calculated at the assumption that the reaction follows the pathway B. This also indicates that the contribution of the S_N2 reaction path to diethyltrichloromethylphosphine (**3a**) is very small. The rate of the formation of the phosphine **3a** was calculated according to Equations 11 and 12 (see appendix) which were brought out on the bases of the Scheme 9.

$$\underset{\substack{\mathbf{3}\\ a\text{-}x\text{-}y}}{R_2PH} + \underset{a\text{-}x\text{-}z}{CCl_4} \xrightarrow{k_1} \underset{\substack{\mathbf{6}\\ x\text{-}y+z}}{R_2PCl} + \underset{x}{CHCl_3} \qquad (1)$$

$$\underset{\substack{\mathbf{6}\\ x\text{-}y+z}}{R_2PCl} + \underset{\substack{\mathbf{5}\\ a\text{-}x\text{-}y}}{R_2PH} \xrightarrow{k_2,\ N(C_2H_5)_3} \underset{\substack{\mathbf{18}\\ y\text{-}z}}{R_2PPR_2} + \underset{y}{\overset{+}{H}N(C_2H_5)_3\ Cl^-} \qquad (2)$$

$$\underset{\substack{\mathbf{18}\\ y\text{-}z}}{R_2PPR_2} + \underset{a\text{-}x\text{-}z}{CCl_4} \xrightarrow{k_3} \underset{\substack{\mathbf{3}\\ z}}{R_2PCCl_3} + \underset{\substack{\mathbf{6}\\ x\text{-}y+z}}{R_2PCl} \qquad (3)$$

Below the respective substrates and products are given their concentration after the time t.

Scheme 9

EXPERIMENTAL

Solvents and reagents were purified by conventional methods. ^{31}P-NMR spectra were recorded on a FT Jeol FX-60 spectrometer operating at 24.3 MHz using 85% H_3PO_4 as an external standard. ^{1}H-NMR spectra were taken on a Tesla BS 487C spectrometer using TMS as an internal standard. IR spectra were recorded on a Specord 71 IR (C. Zeiss) spectrophotometer.

Reaction of diethylphosphine (**5a**) *with carbon tetrachloride and triethylamine in methanol-methylene chloride (2:1/v:v) solution.*

To the stirred solution of carbon tetrachloride (0.17 g, 1.1 mM) and triethylamine (0.12 g, 1.1 mM) in methanol (1.6 ml) a solution of diethylphosphine (**5a**) (0.1 g, 1.1 mM) in methylene chloride (0.8 ml) was added dropwise under argon and the mixture was set aside under argon atmosphere for 24 h at 20°C. Then solvents were evaporated from the reaction mixture to afford the mixture of diethylphosphine oxide (**13a**) ($\delta_{^{31}P}$ = 38.6 ppm), methyl diethylphosphinate (**14a**) ($\delta_{^{31}P}$ = 60.7 ppm) and dichloromethyldiethylphosphine oxide (**15a**) ($\delta_{^{31}P}$ = 55.2 ppm). Molar ratio of these products based on the integrated ^{31}P-NMR, as well as ^{1}H-NMR (see Table I) signals of the crude reaction mixture, is shown in Table I. The individual compounds have been isolated from the mixture by flash chromatography (silica gel; benzene, ethyl acetate, ethanol (3:3:2/v:v:v) and compared (^{1}H-NMR and IR) with authentic samples of diethylphosphine oxide (**13a**),[19] methyl diethylphosphinate (**14a**)[20] and dichloromethyldiethylphosphine oxide (**15a**),[21] respectively. Physical and spectroscopic data of the isolated compounds: **13a**, **14a** and **15a** are presented in Table I.

Rate of formation of diethyltrichloromethylphosphine (**3a**).

A. Reaction of diethylphosphine (**5a**) *with carbon tetrachloride and triethylamine in methylene chloride without added chlorodiethylphosphine* (**6a**). The methylene chloride solution (50 ml) of carbon tetrachloride (2.31 g, 15 mM), triethylamine (1.52 g, 15 mM) and diethylphosphine (**5a**) (1.36 g, 15 mM) was stirred for 3h under argon at 0°C (0.02°C). During this period 2 ml samples were taken at respective time intervals, added to methanol (2 ml) and set aside for 24 h at room temperature under normal atmosphere to oxygenate unreacting starting phosphine. Then the samples were acidified with ethyl ether saturated with hydrogen chloride (0.5 ml) and evaporated under reduced pressure (35°C, 10_{tor}, 15 min). Subsequently samples were taken for qualitative and quantitative analysis of the products using ^{31}P- and ^{1}H-NMR measurements as described above. The samples were shown to consist of diethyl-

phosphine oxide (**13a**), methyl diethylphosphinate (**14a**) and dichloromethyldiethylphosphine oxide (**15a**). The molar amount of dichloromethylphosphine oxide (**15a**) in a sample was assumed to be equal of the molar amount of the formed diethyltrichloromethylphosphine (**3a**).[5] The time dependent molar ratio of diethyltrichloromethylphosphine/starting diethylphosphine, y/a, is recorded in Figure 1.

B. Reaction of diethylphosphine (**5a**) *with carbon tetrachloride and triethylamine in methylene chloride in the presence of added chlorodiethylphosphine* (**6a**). The reaction was carried out as described above but in the presence of 2.5, 7.2 and 10.9 mol% of chlorodiethylphosphine as an addition, respectively. The reaction samples were analyzed qualitatively and quantitatively, similarly as in experiment A. The time dependent molar ratio of diethyltrichloromethylphosphine/starting diphosphine, y/a, for each individual concentration of chlorophosphine used, is recorded in Figure 1.

APPENDIX

The reaction shown in the Scheme 9 are treated as not reversible. Unreversibility of the reaction 1 and 2 follows from the low chemical affinity of the chlorophosphine **6** to the chloroform chlorine atoms and from the presence of triethylamine in the reaction medium, respectively. The reaction of the type 3 was observed to be reversible usually above 100°C.[28]

Assuming steady state to diphosphine **18** the rate of the formation of the phosphine **3** can be described by the Equation 2. This rate however, as it can be seen from Scheme 9 is controlled by the reaction 1 producing the chlorophosphine **6** (Equation 3).

$$\frac{dz}{dt} = k_2(x - y + z)(a - x - y) \tag{2}$$

$$\frac{dx}{dt} = k_1(a - x - y)(a - x - z) \tag{3}$$

Since k_1 is very much less than k_2 and k_3, it may be assumed that the chlorophosphine **6a** is produced mostly by the reaction 1,

$$x >> z - y \tag{4}$$

and its concentration remains small in comparison with the concentration of the final phosphine **3a**, as well as triethylamine hydrogen chloride.

$$z \simeq y >> x \tag{5}$$

If the following simplications are considered:

$$x - y + z \simeq x \tag{6}$$

$$a - x - y \simeq a - x - z \simeq a - y \tag{7}$$

and when initial concentration of chlorophosphine is c, the Equations (2) and (3) may be formulated as follows:

$$\frac{dz}{dt} = \frac{dy}{dt} = k_2(x + c)(a - y) \tag{8}$$

$$\frac{dx}{dt} = k_1(a - y)^2 \tag{9}$$

The solution of this equations, after some transformations, express the rate of the formation of diethyltrichloromethylphosphine (**3a**)

$$\frac{dy}{dt} = k_2(a - y)\sqrt{\frac{k_1}{k_2}}\sqrt{a^2 - (a - y)^2 + \frac{k_2}{k_1}c^2} \tag{10}$$

Integration of the equation (10), using the fact that $y = 0$, when $t = 0$ gives:

$$\frac{a\left(1 + \sqrt{1 - \frac{\left(1 - \frac{y}{a}\right)^2}{1 + \frac{k_2}{k_1}\left(\frac{c}{a}\right)^2}}\right)}{(a - y)\left(1 + \frac{1}{\sqrt{\frac{k_1}{k_2}\left(\frac{a}{c}\right)^2 + 1}}\right)} = e^{at\sqrt{k_1k_2}\sqrt{1 + \frac{k_2}{k_1}\left(\frac{c}{a}\right)^2}} \tag{11}$$

When the chlorophosphine **6a** is not added to the reaction mixture—its initial concentration is 0—the rate of the formation of the phosphine **3a** is expressed by the equation.

$$\frac{a + \sqrt{a^2 - (a - y)^2}}{a - y} = e^{at\sqrt{k_1k_2}} \tag{12}$$

The kinetical curves, the time dependent molar ratio of diethyltrichloromethylphosphine/diethylphosphine, y/a, have been calculated on the basis of the Equations (11) and (12) using k_1 and k_2 and the respective concentration of chlorophosphine **6a**.

Calculation of the Reaction Constants k_1 and k_2

The square root, k_1k_2, has been calculated from the Equation (12) after introducing here the appropriate values of the concentration of the reagents and products, as well as of the respective value of the reaction time.

$$k_1k_2 = 1.592 \cdot 10^{-3}\left[\frac{l}{\text{mol} \cdot \text{sek}}\right] \tag{13}$$

Subsequently, the calculated value of the k_1k_2, the appropriate values of the concentration of reagents and products, including the concentration of the chlorophosphine, as well as the pertinent value of the reaction time were introduced into the Equation (11) and each of its sides were calculated separately at the variable value of k_2/k_1. The value at which both sides were equal to each other determined the real ratio of k_2/k_1.

$$k_2{:}k_1 = 436 \tag{14}$$

The rate constants, $k_1 = 0.762 \cdot 10^{-4}$ [*l*/mol·sek] and $k_2 = 3.324 \cdot 10^{-2}$ [*l*/mol·sek] have been calculated from the Equations (13) and (14).

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