SOLVOLYSIS OF CHLORODIALKYLAND DIARYLPHOSPHINES, DIALKYL PHOSPHOROCHLORIDITES AND DIALKYL PHOSPHINYL CHLORIDES

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The kinetics of solvolysis of chlorodiethylphosphine, chloro(di-n-propyl)phosphine and chlorodiphenylphosphine was studied by conductometry in pure ethanol and in various mixed solvents, and was compared with that of dialkyl phosphorochloridites and of dialkyl and diaryl phosphinyl chlorides. The rate of ethanolysis of chloro(di-n-propyl)phosphine was found to be larger at higher initial concentrations. Addition of sulfuric or perchloric acid enhanced the rate of solvolysis, while sodium perchlorate and lithium chloride had no influence. In ethanol containing water, the rate of solvolysis of chloro(di-n-propylphosphine is approximately proportional to the concentration of water. In formic acid, the solvolysis of chloro(di-n-propyl)phosphine is slower than in ethanol. Addition of acetone to ethanol increases the rate of solvolysis of chloro(di-n-propyl)phosphine—possibly due to a condensation reaction producing a 1-chloroalkyl dialkylphosphine oxide. The rate of ethanolysis of chloro(di-n-propyl)phosphine is considerably enhanced in the presence of isobutylamine, di-n-butyl-amine and triethylamine. The solvolysis of di-t-butylphosphinyl chloride in absolute ethanol is very much slower than that of dimethyl and diethyl phosphinyl chloride.

INTRODUCTION

The solvolysis of organophosphorus halides has been the subject of many studies. At tetracoordinated phosphorus atoms, reactions with nucleophilic reagents were found to proceed both by bimolecular mechanisms,[1-4] sometimes involving pentacovalent intermediates,[5] or by unimolecular mechanisms, with rate determining dissociation of the phosphorus–halogen bond.[6,7] The mechanisms of reactions of tervalent phosphorus compounds, such as of the phosphinous chlorides (chlorodialkylphosphines), R_2PCl, have been less studied, in spite of their importance as highly reactive chemical intermediates. The preparation, properties and reactions of phosphinous chlorides and of phosphinyl chlorides $R_2P(O)Cl$ have been reviewed.[8,9] Chlorodiethylphosphine $(C_2H_5)_2PCl$ and diethyl phosphorochloridite $(C_2H_5O)_2PCl$ have been proposed as useful reagents and intermediates.[10,11] In the present work, the solvolysis of several chlorodialkyl- and diarylphosphines, dialkyl phosphorochloridites and dialkyl phosphinyl chlorides was studied. Because of the rather fast reaction rates encountered, the conductivity method was used.

P.S.—E

RESULTS

1. Solvolysis of chlorodiethylphosphine

A conductometric measurement of the kinetics of solvolysis of chlorodiethylphosphine in dry ethanol at 0°C showed an initial rapid rise in conductivity, which then decreased only slowly. The first order rate constants for the two stages of the reaction were 2.3×10^{-4} and $0.1 \times 10^{-4}\,\text{sec}^{-1}$. In order to find out whether one of these stages could be the solvolysis of diethylphosphinyl chloride present as an impurity in the sample used, the rate of ethanolysis of pure diethylphosphinyl chloride was determined for comparison. As described below (Section 5.1), its rate was very fast, and depending on its initial concentrations, amounted to 6×10^{-4} to $20 \times 10^{-4}\,\text{sec}^{-1}$ Thus it may be that in the ethanolysis of the sample of chlorodiethylphosphine, the initial fast stage is due to the impurity of the phosphinyl chloride, while the slow stage is due to the true solvolysis of chlorodiethylphosphine. An alternative mechanism could involve an ethanolysis to $\text{Et}_2\text{P(OEt)}$, followed by rate-determining reaction of HCl to produce $\text{Et}_2\text{P(O)H}$:

$$\text{Et}_2\text{PCl} + \text{EtOH} = \text{Et}_2\text{POEt} + \text{HCl} \tag{1}$$

$$\text{Et}_2\text{POEt} + \text{HCl} = \text{Et}_2\text{P(O)H} + \text{EtCl} \tag{2}$$
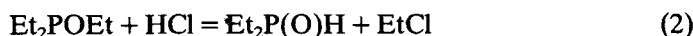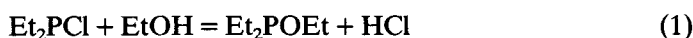
However, such a scheme may be excluded, because it required that the chlorine atom ended up as ethyl chloride, which would extensively evaporate (b.p. 12.2°C). Also, titrimetric checks proved that the amount of chloride ion produced (checked by titration with AgNO_3) was equivalent to the amount of acid formed (NaOH titration). The reaction may thus be described by the above reaction (1), followed by an Arbusow-type of rearrangement to triethyl phosphine oxide:

$$\text{Et}_2\text{POEt} = \text{Et}_2\text{P(O)} \tag{3}$$

2. Solvolysis of chloro(di-n-propyl)phosphine

The rate of solvolysis of chloro(di-n-propyl)phosphine was measured in absolute ethanol, in ethanol containing ether or water or acetone or several amines, and also in wet formic acid. The reaction in absolute ethanol, in an ethanol—ether mixture and in wet formic acid observed first order kinetics (see Table I).

TABLE I

Solvolysis of chloro(di-n-propyl)phosphine. First order rate constants $10^4 k_1\,\text{sec}^{-1}$. Absolute ethanol had been distilled from sodium and ethyl phthalate. Dry ethanol was distilled from CaO. EtOH-ether = Absolute ethanol–diethyl ether (40:60 by volume)

Temp. °C	Abs. ethanol	Dry ethanol	EtOH-ether	HCOOH wet
0	5.4	8.6	4.1	
25.1	36	42.1		15.9
40.1	68	112		

TABLE II

Solvolysis of chloro(di-n-propyl)-
phosphine at different initial con-
centrations in absolute ethanol and
in ethanol containing water at 0°C

n-Pr$_2$PCl Mmolar	Added H$_2$O M	k_1 × 10^4
0.8	—	4.7
3.8	—	5.4
4.2	—	6.6
9.6	—	8.4
27.0	—	14.0
46.0	—	23.0
4.2	0.10	13.7
3.2	0.98	62
6.5	1.00	69
30.0	0.98	87

2.1. *Effects of water.* The solvolysis of chloro(di-n-propyl)phosphine in ethanol is very sensitive to traces of water, as shown by the results of Table I—in which the rates in absolute ethanol (prepared by the more rigorous ethyl phthalate–sodium drying method) were significantly lower than those in ethanol dried only by distilling from lime. In aqueous ethanol (ethanol–water, 90:10 by volume) the rate became too fast to measure at 0°C. Addition of water resulted in steep increases in the rates of solvolysis, as shown in Table II. A plot of first order rate constants against the concentration of water is roughly linear, indicating first order with respect of water (see Figure 1).

2.2. *Salt and acid effects.* In a series of kinetic runs at different concentrations of chloro(di-n-propyl)phosphine, the rate of solvolysis was larger at higher initial concentration, as shown in Table II. In order to find out if the higher rate of reaction at higher initial concentration was due to catalysis by one of the reaction products, the effects of added chloride and hydrogen ions was determined. In the presence of lithium chloride or sodium perchlorate, the rate of ethanolysis was similar to that in pure ethanol for the same initial concentration of the chlorophosphine (see Table IV), proving that the chloride or perchlorate ions do not act as a catalyst. On the other hand, in the presence of added sulfuric or
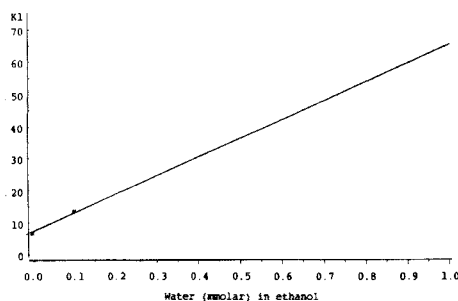

FIGURE 1   First order rate constant 10^4 × k_1 sec^{-1} as a function of concentration of added water in ethanol in the solvolysis of chloro(di-n-propyl)phospine (initially 4–6 mM) at 0°C.

TABLE III

Second order rate constants, lit mol^{-1} sec^{-1}, for the aminolysis of phosphorus chlorides. Data for chloro(di-n-propyl)phosphine, R_2PCl, are for ethanol solvent at 0°C; those for di-iso-propyl phosphorochloridate, $(RO)_2P(O)Cl$, are in benzene at 25°C

Amine	R_2PCl	$(RO)_2P(O)Cl$
Di-n-butylamine	0.06	0.0006
Isobutylamine	0.7	0.066

TABLE IV

Effect of added salts on the ethanolysis of chloro(di-n-propyl)phosphine at 0°C

n-Pr$_2$PCl Mm	Salt added	Conc Mm	$k_1 \times 10^4$ sec^{-1}
4.2	—	—	6.6
27	—	—	11.3
46	—	—	23
5.3	NaClO$_4$	2.4	7.0
9.0	LiCl	3.4	9.4
58	LiCl	3.4	25

TABLE V

Acid catalysis in the ethanolysis of chloro(di-n-propyl)phosphine at 0°C. Values for H^+ are hydrogen ion concentrations at $t_{1/2}$

n-Pr$_2$PCl mM	Acid added	Concn	H^+ Mm	$10^4 \times k_1$ sec^{-1}
0.78	—	—	0.39	4.7
3.8	—	—	1.9	5.4
9.6	—	—	4.8	8.4
27.0	—	—	13.5	13.5
46.0	—	—	23.0	23.0
4.2	H$_2$SO$_4$	0.012	14	18.2
12.0	HClO$_4$	0.020	26.0	22.0
25.4	H$_2$SO$_4$	0.041	54.0	28.0

perchloric acid, marked increases in solvolysis rates were observed (see Table V). Thus, acid catalysis is definitely indicated. As shown in Figure 2, the first order rate constant for the solvolysis at low acidities was approximately linear with the acid concentration. However, the rate reached saturation at higher concentrations of acid. Possibly this saturation was due to incomplete dissociation of sulfuric acid at higher concentrations in ethanol. Acid catalysis had not been found in the solvolysis of dialkyl phosphorochloridates,[1] but did occur in the solvolysis of dialkyl phosphorofluoridates.[12] Hence the higher solvolysis rates observed with larger initial concentrations of the chlorophosphine could be due to catalysis by the acid released during the solvolysis.
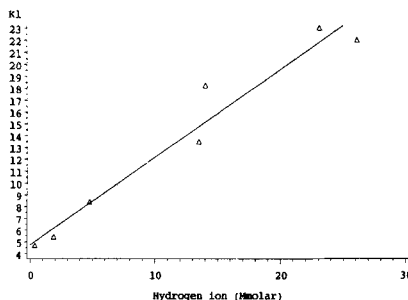
FIGURE 2   First order rate constant $10^4 \times k_1 \sec^{-1}$ versus H^+ concentration in the solvolysis of chloro(di-n-propyl)phosphine in ethanol at 0°C.

2.3. Effects of amines.

In absolute ethanol (dried only by distilling from CaO) in the presence of 13.4 mM triethylamine (which had been distilled from phosphoric anhydride), the first order rate constant for the solvolysis of chloro(di-n-propyl)phosphine (initial concentrations 3.2 mM) was $16 \times 10^{-4} \sec^{-1}$. The reaction was thus twice as fast as in the absence of the amine. In the presence of 100 mM isobutylamine, the ethanolysis of chloro(di-n-propyl)phosphine was almost instantaneous at 0°C. In more dilute solutions of the amine (19 mM) and of the chlorophosphine (37 mM), the rate became measurable at 0°C, the half time for the increase in conductivity being about 10 minutes. In this dilute solution, aminolysis and ethanolysis occurred simultaneously. The relative extent could be determined by acidimetric titration, since alcoholysis neutralizes one equivalent of amine, while aminolysis neutralizes two equivalents. With di-n-butylamine the reaction was slower than with isobutylamine, as shown in Table III, which includes a comparison of the second order rate constants for the aminolysis of the chlorophosphine with those of diisopropyl phosphorochloridate in benzene solution.[1]

2.4. Effects of acetone.

On reacting chloro(di-n-propyl)phosphine at 0°C with a mixture of acetone and ethanol (2:35 by volume), the first order rate constant for the solvolysis was initially $9.0 \times 10^{-4} \sec^{-1}$, rising slowly to $12.3 \times 10^{-4} \sec^{-1}$, while in pure ethanol, the rate constant was $5 \times 10^{-4} \sec^{-1}$. With an even higher concentration of acetone (2:10 ratio of acetone to ethanol), the first order increased from an initial value of 18 to $24 \times 10^{-4} \sec^{-1}$. After several half lives, the conductivity of these reaction solutions dropped considerably, indicating the consumption of the ionic products. A titrimetric assay of such a solution one week later showed that it contained 0.0031 equivalents of acid, but only 0.00033 equivalent of chloride ion. Thus most of the chloride ion must have been incorporated into the product of some reaction between acetone and the chlorophosphine. Such a discrepancy between chloride and acidity production did not occur in the absence of acetone.

3. Solvolysis of chlorodiphenylphosphine

The solvolysis of chlorodiphenylphosphine was found to proceed much faster than that of chloro(di-n-propyl)phosphine. Even at 0°C, dissolving a droplet of chlorodiphenylphosphine in absolute ethanol resulted in a conductivity increase

which corresponded to almost complete solvolysis. For the remaining increase in conductivity, which reached equilibrium after about half an hour, the first order rate constant was $16 \times 10^{-4} \, \text{sec}^{-1}$. For the ethanolysis of diphenyl phosphinyl chloride at 0°C, the rate constant had been reported[1] to be $13 \times 10^{-4} \, \text{sec}^{-1}$. Thus, possibily the relatively slow tail in the solvolysis of our sample of chlorodiphenyl phosphine was due to the alcoholysis of an impurity of diphenyl phosphinyl chloride. Since the boiling points of the two compounds are rather close, e.g. 180° and 222° at 16 torr for Ph_2PCl and $Ph_2P(O)Cl$, respectively, separation is difficult. In order to decrease the initial fast rate of solvolysis of chlorodiphenylphosphine, the ethanol was diluted with ether. At 0°C, in an ethanol–ether mixture (40:60 parts by volume), the first order rate constant was still very high, in the range of 20×10^{-4} to $70 \times 10^{-4} \, \text{sec}^{-1}$.

4. Solvolysis of dimethyl and diethyl phosphorochloridite

The reaction of diethyl phosphorochloridite with sodium ethoxide had been shown to produce triethyl phosphite.[13] On the other hand, in the solvolysis of the phosphorochloridite in ethanol, the product could be either diethyl ethylphosphonate, formed by the reaction,

$$(EtO)_2PCl + EtOH \rightarrow (EtO)_2P(O)Et + HCl \qquad (4)$$
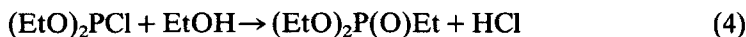
one equivalent of acid and of chloride ion being formed for each mole of the phosphorochloridite, or alternatively there could be initial production of triethyl phosphite, which could then decompose either to diethyl ethylphosphonate and HCl, or to diethyl phosphine oxide $(EtO)_2P(O)H$ and ethyl chloride. An attempt to resolve this question by measurement of the infrared absorption of the reaction product was inconclusive. The observed strong infrared absorption band at $1253 \, \text{cm}^{-1}$, due to the $P{=}O$ stretching vibration, seems to favor the $(EtO)_2P(O)H$ structure, for which the value $v_{P{=}O} = 1260 \, \text{cm}^{-1}$ was previously found.[14] However, the analysis of the reaction products indicated that the amount of chloride ion and acidity produced are equivalent, as required by the overall reaction (4) above.

Attempts to measure the rate of ethanolysis of dimethyl and diethyl phosphorochloridite by the batch conductivity method showed that the reaction is practically instantaneous at 0°C. With diethyl phosphorochloridite at −61° and at −80°C, it was possible to get a rough indication of the rate (see Table VI), but

TABLE VI

Solvolysis of diethyl phosphorochloridite. EtOH–EtOEt = Ethanol–Ether (1:9 by volume)

Temp. °C	$(EtO)_2PCl$ mM	Solvent	Method	k_1 sec^{-1}
−80	7.8	Ethanol	Conduct.	0.6×10^{-4}
−80	5.1	Ethanol- 0.1M i-BuNH$_2$	Conduct.	0.3×10^{-4}
−65		Ethanol	Conduct	2×10^{-4}
20	4	EtOH–EtOEt 2mM NaOEt	Flow	30

because of the difficulties of conductivity measurements at such temperatures (high viscosity and resistance), the results were of poor precision. In the presence of an excess of isobutylamine, the rate of solvolysis of diethyl phosphorochloridite at −80° was similar to that in ethanol alone, within the experimental error (see Table VI). Thus, there was no base catalysis in its solvolysis. In this respect the solvolysis of diethyl phosphorochloridite differed from that of chloro(di-n-propyl)phosphine, as reported above (Section 2.3).

An order of magnitude value for the rate of solvolysis of diethyl phosphorochloridite at room temperature in mixtures of ethanol–diethyl ether could be determined using a tubular flow reactor (see Experimental). The extent of reaction along the tube was measured by visual observation of the color change of an acid-base indicator at the point corresponding to the half-time. This visual method is based on the above observation of lack of base catalysis in the solvolysis of diethyl phosphorochloridite. Thus, on mixing a stream containing a solution of diethyl phosphorochloridite (4.0 mM) in dry ether with another stream consisting of a solution of sodium ethoxide (2.0 mM) in ethanol–ether (1:4 by volume), at a driving pressure of 10 lb/sq. in. and a total flow rate of 12 ml sec^{-1} in a reaction tube of 0.10 cm radius resulted in a change of color of the indicator (phenolphthalein) at 9 cm distance from the mixing chamber. Since the initial concentration of the ethoxide was just one half of the initial concentration of the phosphorochloridite, the point of color change according to Equation (1) above corresponded to the half time, which was therefore 0.023 s and the first order rate constant $30 s^{-1}$. The color change of the indicator was not very clear, and the result provides only an order of magnitude of the rate.

5. Solvolysis of dialkylphosphinyl chlorides

5.1. Diethylphosphinyl chloride.
The rate of ethanolysis of diethylphosphinyl chloride was found to depend on the initial concentration of the material, as shown in Table VII. Within each run, quite good adherence to first order kinetics was observed. However, between different runs, considerable differences were

TABLE VII

Solvolysis of diethylphosphinyl chloride in absolute ethanol as a function of its initial concentration and of added water. Temperature: 0°C.

Et$_2$POCl M	H$_2$O M	$k_1 \times 10^4$ sec^{-1}
0.0025	—	6.1
0.0035	—	6.7
0.0065	—	6.5
0.0065	—	9.6
0.0082	—	8.2
0.042	—	19.4
0.017	0.98	66

TABLE VIII

First order rate constants for the sol-
volysis of di-t-butylphosphinyl chloride

Temp. °C	Solvent	k_1 sec^{-1}
40.1	Abs. Ethanol	0.47×10^{-7}
40.1	80% Ethanol	0.33×10^{-4}

obtained. This was probably not due to the entrance of moisture, because it was necessary to have a 1 M solution of water in ethanol in order to increase the rate of solvolysis ten times (see Table VII). In a redetermination of the solvolysis of very carefully purified diethylphosphinyl chloride in dry ethanol at 0.2°C, the rate constant was found to be 6.8×10^{-4} sec^{-1}.

5.2. Solvolysis of di-t-butylphosphinyl chloride. The determination of the kinetics of solvolysis of di-t-butylphosphinyl chloride was undertaken in order to compare the rate with that of diethylphosphinyl chloride (above), and with that of dimethyl- and diphenylphosphinyl chloride reported previously.[1] The change in structure of the phosphinyl chloride from dimethyl- to di-t-butyl- may possibly, in reactions with nucleophilic reagents, facilitate the formation of a transition state involving ionization of the P–Cl bond. On the other hand, it is likely to impede the extent of bonding between the nucleophilic center of the reagent and the phosphorus atom—which determines the transition state in a bimolecular mechanism. Results for the solvolysis of di-t-butylphosphinyl chloride in absolute ethanol and in 80% ethanol (20% water) at 40.1°C are shown in Table VIII, and indicate extremely slow reaction rates.

DISCUSSION

The decrease in the rates of solvolysis of the dialkylphosphinyl chlorides in the series $Me_2P(O)Cl$, $Et_2P(O)Cl$ and $t\text{-}Bu_2P(O)Cl$, as indicated in Table IX, is in agreement with a mechanism of bimolecular nucleophilic displacement, SN_{II}, with rate–determining bond-formation between a nucleophilic reagent and the phosphorus atom, involving pentacovalent phosphorus either as a transition state,[1-4] or as an intermediate.[5] The previously observed absence of ^{18}O-exchange during the hydrolysis of diethylphosphinyl chloride[2] indicated that even if a pentacovalent phosphorus atom were involved, the two OH proups of such an intermediate are not sterically equivalent.

In the chlorodialkylphosphines and the dialkyl phosphorochloridates, the tervalent phosphorus atom is the site of a pair of non-bonding electrons. The predominant observed feature in the solvolysis of chloro(di-n-propyl)phosphine is the catalytic effect of acids and of triethylamine, as well as the very fast reactions with primary and secondary amines. A tentative mechanism therefore involves both acid and base catalysis, with proton transfer as the primary step. The rates of ethanolysis of chlorodiethylphosphine and of chloro(di-n-
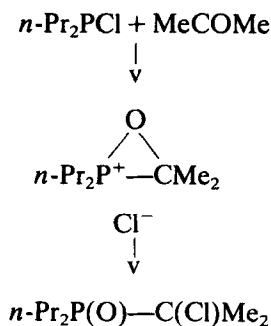
TABLE IX

Comparison of ethanolysis of several groups of phosphorus chlorides at 0°C; first order rate constants $k_1 \times 10^4 \, \text{sec}^{-1}$. Data marked* are extrapolated from other temperatures

	(MeO)$_2$PCl v. fast	Me$_2$POCl 120*	(MeO)$_2$POCl 0.56
Et$_2$PCl 0.1 n-Pr$_2$PCl 4.7	(EtO)$_2$PCl v. fast	Et$_2$POCl 6.8	(EtO)$_2$POCl 0.23
			(i-PrO)$_2$POCl 0.10
		t-Bu$_2$POCl v. slow	
Ph$_2$PCl v. fast		Ph$_2$POCl 13	(PhO)$_2$POCl 0.5*

propyl)phosphine are slower than that of diethyl phosphinyl chloride (see Table IX). Thus, the decreased positive charge at the phosphorus atom of the chlorphosphine relative to the phosphinyl chloride causes decreased reactivity towards nucleophilic reagents. The rather slow rate of solvolysis of chloro(di-n-propyl)phosine in formic acid indicates that the rate determining step is not likely to be an ionization process.

The enhancement in the rate of solvolysis of chloro(di-n-propyl)phosphine in the presence of acetone may presumably be due to the formation of an α-chloroalkylphosphine oxide as an addition product. Condensation reactions between chlorodialkylphosphines and aldehydes and ketones have been previously studied.[10,15] The condensation may presumably have occurred according to the following scheme, possibly involving a Michaelis–Arbusov rearrangement with a phosphonium chloride intermediate, the occurrence of which may explain the large initial increase in conductivity:

$$n\text{-Pr}_2\text{PCl} + \text{MeCOMe}$$

$$\downarrow$$

$$n\text{-Pr}_2\text{P}^+\!\!\overset{\displaystyle O}{\overset{\displaystyle /\;\;\backslash}{-}}\!\!\text{CMe}_2$$

$$\text{Cl}^-$$

$$\downarrow$$

$$n\text{-Pr}_2\text{P(O)}\!-\!\text{C(Cl)Me}_2$$

EXPERIMENTAL

Dichloroethylphosphine was prepared according to Kharash *et al.* from phosphorus trichloride and tetraethyl lead.[16]

Chlorodiethylphosphine was obtained from dichloroethylphosphine and tetraethyl lead according to Beeby and Mann.[17] B.p. 129–130°C. Found, Cl, 28.6. Calc. for $C_4H_{10}ClP$: Cl, 28.5%.

Tri-n-propyl phosphine oxide was prepared according to Davies and Jones,[18] b.p. 100–111°C/2 torr, colorless hygroscopic crystals.

Chloro(di-n-propyl)phosphine was prepared from tri-n-propyl phosphine oxide and phosphorus pentachloride.[19] B.p. 95°C/2 torr, a colorless liquid. Found, Cl, 20.8; $C_6H_{17}ClP$ requires Cl, 23.3%.

Chlorodiphenylphosphine was prepared according to Michaelis[20] from phenyl dichlorophosphine and diphenyl mercury. B.p. 133–7°C/2 torr, a colorless oil. Found Cl, 16.3; $C_{12}H_{10}ClP$ requires Cl, 16.1%.

Diethylphosphinyl chloride. Diethylphosphinic acid was prepared according to Kosolapoff and Watson,[21] by adding bromine (50 ml of 0.4 M bromine in carbon tetrachloride) dropwise to chlorodiethylphosphine (1.45 g). A white precipitate formed. Water was added in excess and the mixture was evaporated on the steam bath. The residual oil was dried at 100° under vacuum. Benzene (10 ml) and phosphorus pentachloride (2.4 g) was added and the mixture was refluxed on the steam bath for an hour, with exclusion of moisture. The solution was then twice vacuum distilled. B.p. 95°C/8 mm, yield 0.5 g (31%); a colorless clear liquid. Found, Cl, 25.7. Calc. for $C_4H_{10}OClP$; Cl, 25.3%.

Di-t-butylphosphinic acid was obtained as described by Crofts and Kosolapoff,[22] m.p. 204–6°C Found: Equiv. wt. by titration with NaOH (phenolphthalein): 179. C, 54.6; H, 11.0; P, 17.7%. Calc. for $C_8H_{19}O_2P$: Equivl wt. 178; C, 54.0; H, 10.7; P, 17.4%.

Di-t-butylphosphinyl chloride was prepared by refluxing di-t-butylphosphinic in benzene solution with an excess of phosphorus pentachloride for 2 hours. After evaporation under reduced pressure crystals remained, which could be sublimed in vacuum. Approximate m.p. of the hygroscopic crystals: 34–6°C. Found: Cl, 22.7. $C_8H_{18}OClP$ requires Cl, 18.1%.

Diethyl phosphorochloridite was prepared according to Cook *et al.*[23] B.p. 59–61°C/34 torr. Found: Cl 22.6%. Calculated for $C_4H_{10}O_2ClP$: Cl, 22.7%. A recent procedure is that by Majevski.[9]

Dimethyl phosphorochloridite was prepared by the same procedure as for diethyl phosphorochloridite. B.p. 25–26°C/29 torr. Found: Cl, 24.1 Calc. for $C_2H_6O_2ClP$: Cl, 27.6%.

Kinetic measurements. Reaction rates were determined from the changes in conductivity, as previously described.[1]

Flow reactor. The driving force was a compressed nitrogen tank with reducing valve and meter reading to 1 lb/sq. in. A steel barrel served as pressure equalizer, and an 80 cm high mercury column as a safety valve. Two round-bottomed thick-walled glass flasks (100 or 200 ml) closed with rubber stoppers served as reactant containers. Two glass tubes passed through each stopper, one short—to apply pressure, and one going down to the bottom of the flask. The mixing chamber was a capillary T tap of 2.0 mm inner diameter.[24] The tap was kept pressure tight by a spring clamp. The outlet from the tap perpendicular to the two others was lengthened to 71 cm with 2.0 mm capillary glass tubing. This section served as the flow reactor. It was kept in a vertical upward position, and the overflowing liquid was collected through a short section of rubber tubing into a graduated cylinder. In a tubular flow system, the time τ, in sec, at a given point along the flow tube is related to the distance d, in cm, between the mixing chamber and this point, the radius of the flow tube r, in cm, and the flow rate F, in cm^3 sec^{-1}, by the equation:

$$\tau = \pi d r^2 / F \text{ (in sec}^{-1}) \tag{5}$$

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