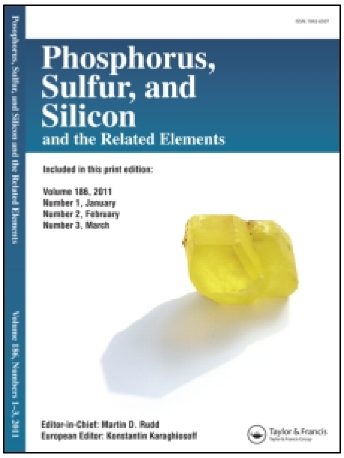

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Investigation Of The Reaction Between Dialkylphosphine Oxides And Carbontetrachloride

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INVESTIGATION OF THE REACTION BETWEEN DIALKYLPHOSPHINE OXIDES AND CARBONTETRACHLORIDE

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The time dependent formation of intermediates and end products in the reaction between $Et_2P(O)H$ and CCl_4 is analysed using ^{31}P-NMR technique. The various reaction steps are studied separately in order to elucidate the overall mechanism. A key step is the disproportionation of $Et_2P(O)H$ catalysed by Et_2PCl and $Et_2P(O)Cl$, in a cyclic process, the latter being produced initially by the reaction between $Et_2P(O)H$ and CCl_4. The diethylphosphine formed during disproportionation reacts immediately with CCl_4, driving the reaction through the intermediates, Et_2PCl and Et_2PCCl_3 which react with $Et_2P(O)OH$ producing $Et_2P(O)Cl$, $(Et_2PO)_2O$, and $Et_2P(O)CHCl_2$, as end products.

The influence of the substituents on rate and product yields was studied with *n*-propyl, *n*-butyl, *n*-octyl, and allyl as substituents in the dialkylphosphine oxide.

Dialkylphosphine oxides are reported to react with carbontetrachloride in the presence of ethanol, forming dialkylphosphinates.[1] The mechanism might be similar to the corresponding one between dialkylphosphites and CCl_4, where $(RO)_2P(O)Cl$ is assumed to be formed as intermediate.[2] In the absence of ethanol dialkylphosphinic acid has been isolated.[3] As part of a general mechanism the formation of $R_2P(O)Cl$ in the latter reaction seems likely since Seel and Velleman have brought strong evidence that dimethylphosphinylchloride[4] takes part in the disproportionation of $Me_2P(O)H$ to $Me_2P(O)OH$. In fact, diphenyl phosphine oxide, which is considerably more stable than the corresponding dialkylphosphine oxide gives rise to $Ph_2P(O)Cl$ as the major product.[5] As dialkylphosphinic acid can be formed from $R_2P(O)H$ during its disproportionation in the presence of oxygen, or from $R_2P(O)Cl$ in the presence of water, it is necessary to take special precaution to exclude oxygen and water from the reaction mixture.

In order to evaluate the mechanism of the above reaction, diethylphosphine oxide (**1**) and CCl_4 were reacted together in carefully dried benzene in an argon atmosphere. Diethylphosphinic acid was still shown to be one of the intermediates, indicating that disproportionation had taken place as one of the reaction steps.

The time dependent formation of intermediates and end products was investigated using ^{31}P-NMR. The compounds were isolated and characterized separately, occasionally compared with authentic samples. In Table I the spectral data of the compounds identified from the reaction mixture are summarized. The time dependent molar ratios of the various intermediates and products are recorded in Table II.

TABLE I

Spectral data of intermediates (**4**), (**6**), (**2**)[a] and end products (**3**), (**5**), (**7**), formed in the reaction between diethylphosphine oxide (**1**) and carbon tetrachloride in benzene

Compounds	^{31}P-NMR	MS[g]	^{13}C-NMR[h]
	δ ppm (80% H_3PO_4ext.)	m/e (rel. int.%)	δ ppm (C_6D_6/TMS int.)
Et_2PCl(**4**)	118 (lit.,[21] 119)	124, 126 (M^+; 33, 11); 96.98($M^+—CH_2=CH_2$; 100, 33)	
$Et_2P(O)Cl$(**3**)	73.8 (lit.,[21] 74.8)	140, 142(M^+; 6.0, 2.0); 112, 114 ($M^+—CH_2=CH_2$ 100, 33); 105 (M^+—Cl, 62)	
$Et_2P(O)OH$(**2**)	64.1–69.0[b](60.9)[c]		5.5(d, $^2J_{PC}$ = 4.5 Hz, —CH_3) 19.7(d, $^1J_{PC}$ = 92.0 Hz, —CH_2—)
$[Et_2P(O)]_2O$(**5**)	61.1(61.7)[d]	227, 226, 225 (M^+ + 1, M^+, M^+ − 1; 1.6, 1, 8); 198, 197 ($M^+—CH_2=CH_2$, M^+ − 1; $CH_2=CH_2$; 24.8, 24.6) 169[M^+-1-2($CH_2=CH_2$); 100], 105($Et_2P(O)^+$; 51)	
$Et_2P(O)CHCl_2$(**7**)	55.9(55.2)[e]	188, 190 (M^+; 2.6, 1.5); 105 ($Et_2P(O)^+$, 100)	65.7 ppm (d, $^1J_{PC}$ = 55.9 Hz, —$CHCl_2$);,
Et_2PCCl_3(**6**)	58.0(58.0)[f]	206, 208, 210 (M^+; 8, 8.3, 2.7); 178, 180, 182 ($M^+—CH_2=CH_2$; 25, 26, 8.1); 150, 152, 154 ($M^+—2CH_2=CH_2$; 100, 100, 30)	10.3 (d, $^2J_{PC}$ = 19.1 Hz, —CH_3) 21.0 (d, $^1J_{PC}$ = 19.1 Hz, —CH_2—) 101.8 (d, $^1J_{PC}$ = 71 Hz,—CCl_3)

[a] The presence of acid among the end products indicates that the reaction mixture has not been entirely protected against oxygen.

[b] Chemical shift is displaced towards lower field with progress of reaction due to increasing amount of HCl.

[c] Authentic specimen (neat).

[d] Authentic specimen in $CHCl_3$.

[e] Isolated compound in $CHCl_3$.

[f] Authentic specimen in CH_2Cl_2.

[g] Recorded after 0.5 h and 2 h, GC/MS (glass column 3% OV^3-17, or glass inlet system).

[h] For ^{13}C-NMR the reaction was carried out in microscale in C_6D_6 at the same concentrations and conditions as the title reaction.

TABLE II

Molar ratios of intermediates and end products formed in the reaction between diethylphosphine oxide (**1**) and carbontetrachloride[a]

Time h	Molar ratios of intermediates and end products					
	Et_2PCl (**4**)	$Et_2P(O)Cl$ (**3**)	$Et_2P(O)OH$ (**2**)	$[Et_2P(O)]_2O$ (**5**)	$Et_2P(O)CHCl_2$ (**7**)	Et_2PCCl_3 (**6**)
0.5	0.06	0.00	0.575	0.08	0.00	0.285
1.5	0.06	0.025	0.55	0.08	0.025	0.26
2.5	0.06	0.085	0.49	0.08	0.085	0.20
5.0	0.05	0.145	0.44	0.08	0.135	0.15
1.8	0.01	0.31	0.28	0.08	0.29	0.00
66.0	0.00	0.37	0.24	0.08	0.31	0.00
140.0	0.00	0.37	0.24	0.08	0.31	0.00

[a] For condition see experimental part.

It is seen that diethylphosphinic acid (**2**), diethylphosphine (**4**), and diethyl-trichloromethylphosphine (**6**) are gradually decreasing. The maximal concentration of these intermediates are formed before the first NMR-measurement is carried out. The end products, diethylphosphinyl chloride (**3**) and diethyl-dichloromethylphosphine oxide (**7**) are continuously increasing, whereas diethylphosphinic acid anhydride (**5**) being practically constant during the reaction course.

When the amount of CCl_4 in the reaction mixture was varied, it was observed that a small amount of CCl_4 was able to initiate the disproportionation process, forming $Et_2P(O)OH$ (**2**) and Et_2PH (**1a**). Since small amount of CCl_4 would be very rapidly consumed in the further reaction with the Et_2PH formed, CCl_4 cannot be the real disproportionation catalyst. However, in the disproportionation of $Me_2P(O)H$ Seel and Velleman have postulated that Me_2PCl as well as $Me_2P(O)Cl$ are involved in the process.[4] It was therefore natural to expect similar involvement of Et_2PCl and $Et_2P(O)Cl$. Figure 1 shows that the latter compounds exhibit identical catalytic

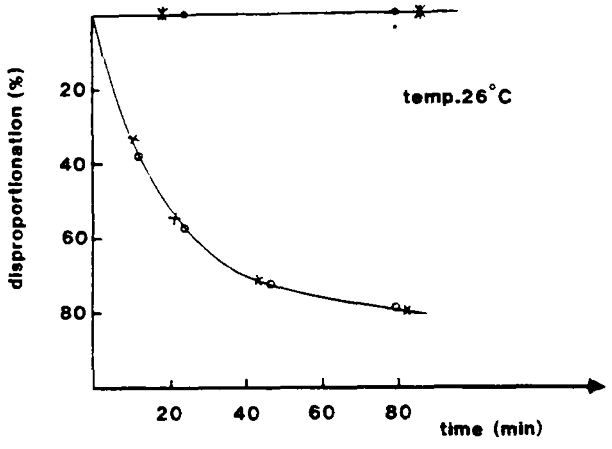
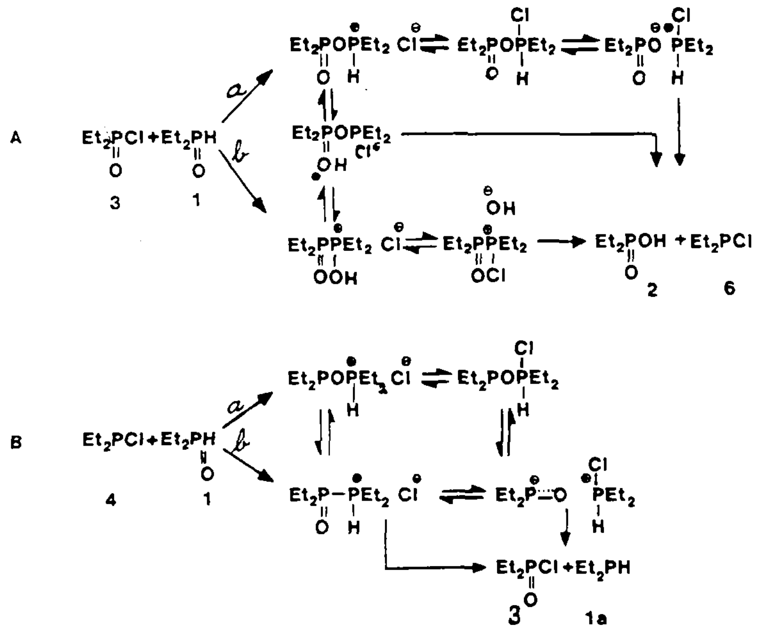


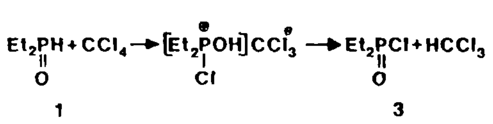
FIGURE 1 Disproportionation of $Et_2P(O)H$ in the presence of 3.15% of × Et_2PCl, ○ $Et_2P(O)Cl$, • HCl, ○ Na.

effect in the disproportionation of $Et_2P(O)H$. From the same figure it is seen that strong acids or bases do not promote the disproportionation reaction. The identical catalytic effect of Et_2PCl and $Et_2P(O)Cl$ can only be understood if both compounds take place in a cyclic reaction path during the disproportionation. A mechanism induced by radicals is highly unlikely since hydroquinone had no effect on the rate of disproportionation. Several ionic reaction routes might be visualized, either by nucleophilic attack of oxygen on phosphorus[7] (route a), or by phosphorus-phosphorus attack[8] (route b) in A and B in Scheme 1:



SCHEME 1

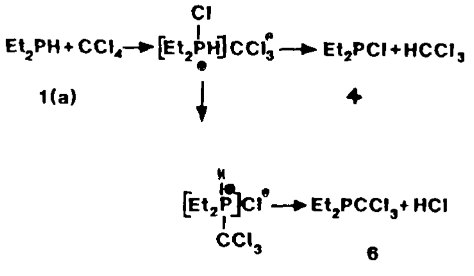
Initially CCl_4 is assumed to participate in the formation of catalytic amount of $Et_2P(O)Cl$ which is necessary for starting the disproportionation of $Et_2P(O)H$ (Scheme 2). Later during the reaction $Et_2P(O)Cl$ as well as the second disproportionation promoting species, Et_2PCl will both be supplied in greater amount as one of the end product ((3), Scheme 4), respectively secondary intermediate ((4), Scheme 4). Scheme 1 presupposes that disproportionation, forming Et_2PH (**1a**) and



$$\underset{\mathbf{1}}{Et_2\underset{\overset{\|}{O}}{P}H} + CCl_4 \rightarrow [Et_2\underset{Cl}{\overset{\oplus}{P}}OH]\overset{\ominus}{C}Cl_3 \rightarrow \underset{\mathbf{3}}{Et_2\underset{\overset{\|}{O}}{P}Cl} + HCCl_3$$

SCHEME 2

$Et_2P(O)OH$ (**2**), must take place before the reaction can proceed further. The highly reactive Et_2PH would be expected to react immediately with CCl_4 producing Et_2PCCl_3(**6**) and Et_2PCl (**4**):



SCHEME 3

A graphical view of the time dependent formation of intermediates and products formed from $R_2P(O)H$ (0.05 M) and CCl_4 (0.052 M) in benzene at 20°C is presented in Figure 2. It indicates that the disproportionation reaction forming $R_2P(O)OH$ and R_2PH, and the latter's reaction with CCl_4 producing Et_2PCl and Et_2PCCl_3 has bypassed their maximum concentrations long before the first measurements (after $\frac{1}{2}$ h) is performed. Strong evidence for this reaction route is obtained by reacting equimolecular amounts of separately synthesized $Et_2P(O)OH$ and Et_2PH with CCl_4 under similar conditions in benzene solution as for pure $Et_2P(O)H$ and CCl_4. In Table III it is seen that an equimolecular mixture of Et_2PH and $Et_2P(O)OH$ in the presence of CCl_4 gives rise to the same products (2)–(7) in

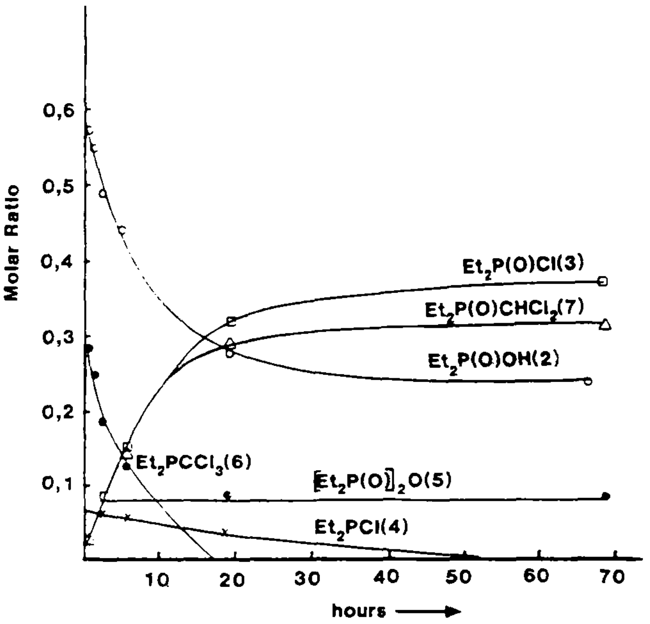


FIGURE 2 The time dependent formation of intermediates and end products in the reaction between $Et_2P(O)H$ (0.05%) and CCl_4 (0.05%) in benzene at 20°C.

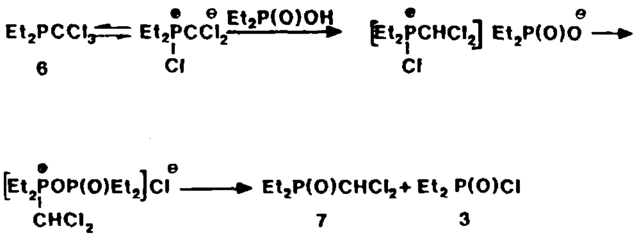
TABLE III

Molar ratios distribution of intermediates and end products formed in the reaction between diethylphosphine (**1a**) diethylphosphinic acid (**2**; and carbontetrachloride.[a]

Time (h)	Molar ratios of intermediates and end products					
	Et_2PCl (**4**)	$Et_2P(O)Cl$ (**3**)	$Et_2P(O)OH$ (**2**)	$[Et_2P(O)]_2O$ (**5**)	$Et_2P(O)CHCl_2$ (**7**)	Et_2PCCl_3 (**6**)
5	0.06	0.15	0.42	0.06	0.16	0.15
18	0.01	0.31	0.30	0.06	0.29	0.00
66	0.00	0.37	0.26	0.06	0.31	0.00

[a] For condition see experimental part.

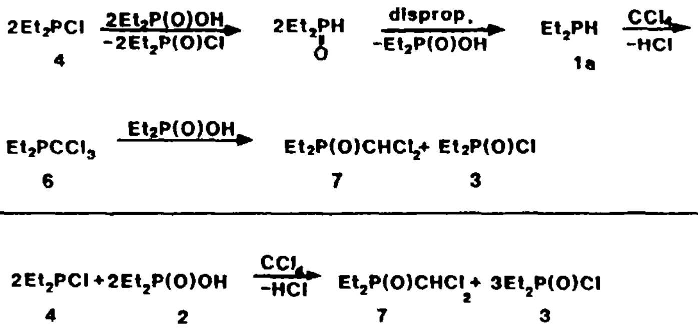
identical molar ratios as the reaction of $Et_2P(O)H$ and CCl_4 (Table II). From Figure 2 it is seen that Et_2PCCl_3 (**6**) and $Et_2P(O)OH$ (**2**) decrease at comparable rates, whereas $Et_2P(O)CCl_2$ is formed at the similar rate as $Et_2P(O)Cl$. This observation indicates that the reactions are interlinked in the following sequences:



SCHEME 4

The reaction path in Scheme 4 was also proved by reacting pure Et_2PCCl_3 with $Et_2P(O)OH$ giving rise to products (**3**) and (**7**) (Table IV).

Due to its high reactivity Et_2PCl has only the character of an intermediate in the overall reaction sequences (Figure 2). It seems highly reasonable that Et_2PCl takes part in the following transformations:



SCHEME 5

TABLE IV

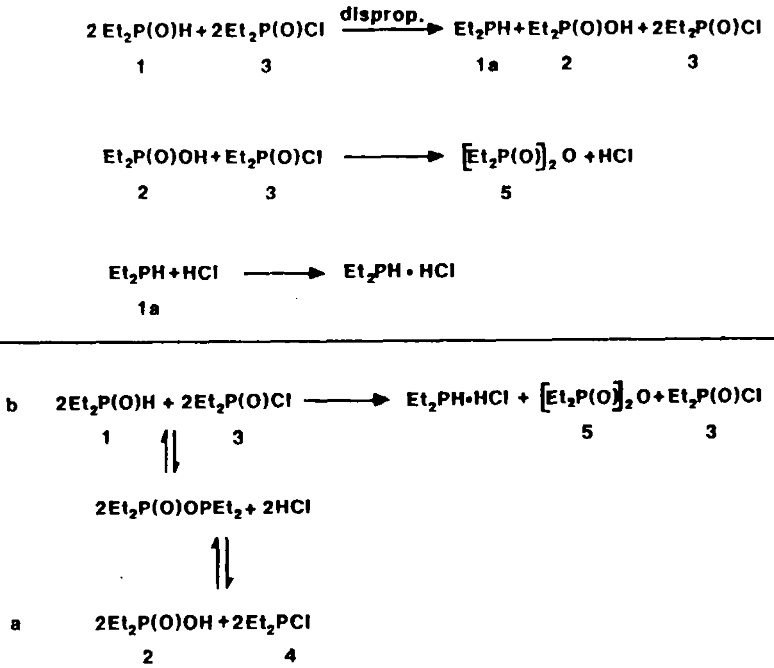
Molar ratios of products formed in the reactions: a) between diethyltrichloromethylphosphine (**6**) and diethylphosphinic acid (**2**); b) between diethylchlorophosphine (**4**) and diethylphosphinic acid (**2**) in the presence of carbontetrachloride

Reaction	Molar ratios of			
	$Et_2P(O)Cl$ (**3**)	$Et_2P(O)OH$ (**2**)	$[Et_2P(O)]_2O$ (**5**)	$Et_2P(O)CHCl_2$ (**7**)
a) Et_2PCCl_3 + $Et_2P(O)OH$ (**6**) (**2**)	0.14	0.22	0.25	0.39
b) Et_2PCl + $Et_2P(O)OH$ + CCl_4 (**4**) (**2**)	0.58	0.17	0.10	0.15

The reaction sequences suggested in Scheme 5 are in accordance with the following experiments carried out with separately synthesized pure compounds: Et_2PCl reacts with $Et_2P(O)OH$ in the *presence* of CCl_4 giving rise to the expected products (Table IV). These products are the same as obtained from Et_2PCCl_3 and $Et_2P(O)OH$ in the absence of CCl_4 (Table IV).

Et_2PCl reacts with $Et_2P(O)OH$ in the *absence* of CCl_4 giving identical products, and product ratios, as the reaction between $Et_2P(O)Cl$ and $Et_2P(O)H$ (Table V).

The latter 2 reactions are considered as part of the reactions outlined in Scheme 5. Their interlinking character is illustrated through reaction Scheme 6 where the quantitative aspect (identical product ratios) are expressed through stoichiometric reaction formulaes:



SCHEME 6

TABLE V

Molar ratios of products formed in the reactions: a) between diethylchlorophosphine (**4**) and diethylphosphinic acid (**2**); b) between diethylphosphine oxide (**1**) and diethylphosphinyl chloride (**3**)

	Molar ratios of			
Reaction	$Et_2P(O)Cl$ (**3**)	$Et_2P(O)OH$ (**2**)	$[Et_2P(O)]_2O$ (**5**)	Et_2PH HCl (**1a**)
a) Et_2PCl + $Et_2P(O)OH$ (**4**) (**2**)	0.07	0.24	0.35	0.24
b) $Et_2P(O)Cl$ + $Et_2P(O)H$ (**3**) (**1**)	0.05	0.25	0.36	0.24

Earlier findings concerning the formation of mixed anhydrides,[23] and the tendency of disproportionation of the P(O)H group under the influence of chlorophosphines[4] are in accordance with Scheme 6. When Table IV and V, and Scheme 5 and 6 are compared, it is seen that CCl_4 is consumed in the reaction with Et_2PH producing chiefly $Et_2P(O)CHCl_2$ and $Et_2P(O)Cl$ instead of $[Et_2P(O)]_2O$ and Et_2PH HCl in its absence.

The influence of the R-substituents on the $R_2P(O)H$ / CCl_4 reaction

In order to evaluate the more general aspects of the $R_2P(O)H/CCl_4$ reaction, the study was extended to comprise $R_2P(O)H$ with R = *n*-propyl, *n*-butyl, *n*-octyl, and allyl substituents. Chromatography (GCL), as well as spectroscopy (^{31}P-, ^{1}H-, ^{13}C-NMR, IR, and MS) was used for identification, isolation, and characterizing reactants, intermediates and end products.

The same spectrum of intermediates and end products were found as observed in the $Et_2P(O)H/CCl_4$ reaction. The ^{31}P-NMR data of the various compounds isolated and characterized are recorded in Table VI. The integrated ^{31}P-NMR absorption peaks were used to follow the time dependent formation of intermediates and end products (Table VII). It is seen that the various dialkylphosphine oxides give rise to corresponding end products, $R_2P(O)OH$, $R_2P(O)Cl$ $[R_2P(O)]_2O$, and $R_2P(O)CHCl_2$ but their time dependent concentrations are quite different, revealing different influences of substituents. Regarding di-octyl- and diallylphosphine oxides, it is seen that the disproportionation process proceeds much slower; 39%, respectively, 70% dialkylphosphine oxide, is still present after 48 hours reaction at room temperature. On the other hand, R_2PCCl_3, formed by the same oxides seems to be less substituent dependent since it has not been observed, and must therefore react much more quickly than it is formed. The different molar ratios of reactants, intermediates, and end products (Table VII), do not point to different reaction routes since no new intermediates and products have been detected.

Spectral data of the various dialkyl dichloromethylphosphine oxides not earlier synthesised are recorded in Table VIII.

EXPERIMENTAL

Instruments used. *^{31}P-NMR Spectra* were recorded at 24.3 MHz using a JNM-C-60 HL spectrometer equipped with heteronuclear spin decoupler, JNM-SD-HC. 85% H_3PO_4 was used as external standard.

TABLE VI

^{31}P NMR data of intermediate and end products formed in the reaction of dialkylphosphinic oxide (**1**) with CCl_4. In brackets are shown data from literature or data isolated or prepared compounds.

R Intermediate and end product	*n*-propyl	*n*-butyl	allyl	*n*-octyl
R_2PCl	109.1	113.8 [116]^{22}	--	110.3
$R_2P(O)Cl$	71.7	70.2 [70.7]^{21}	58.0 [57.7]^{b}	70.7 [71.0]^{b}
$R_2P(O)OH$	63.9–67.2^{a}	62.9–67.0^{a}	48.1–50.2^{a} [45.9]^{d}	64.0–67.8^{a}
$[R_2P(O)]_2O$	62.0	58.50	45.5 [43.2]^{b}	56.7
$R_2P(O)CHCl_2$	53.2 [52.5]^{c}	54.1 [54.0]^{c}	42.5 [42.2]^{c}	51.5 [50.0]^{c}
R_2PCCl_3	48.9 [46.3]^{d}	49.4 [47.5]^{d}	—	—

[a] Chemical shift is displaced towards lower field with the progress of reaction due to the increase of HCl in the reaction mixture, formed in the reaction between $R_2P(O)Cl$ and $R_2P(O)OH$ giving $[R_2P(O)]_2O$, as well as in the reaction between R_2PCl, $R_2P(O)OH$ and CCl_4 (Scheme 5).

[b] See experimental part.

[c] Isolated compounds, see table VIII.

[d] Authentic samples in CH_2Cl_2.[6]

^{1}*H-NMR Spectra* were recorded at 80 MHz with Tesla BS 487 C, or at 60 MHz with Tesla BS 467 Spectrometers, using tetramethylsilane as internal standard. *M.S. Spectra* were recorded on a LKB-9000 mass spectrometer. *IR-Spectra* were recorded on a Specord 71 IR (C. Zeiss) spectrophotometer.

Synthesis of dialkylphosphine oxides. Dialkylphosphine oxides were obtained according to a method of Hayes[9] used for preparation of $Et_2P(O)H$: To a solution of alkylmagnesium halide in THF diethylphosphonate was added followed by the addition of aqueous K_2CO_3 in order to hydrolyse the dialkylphosphinite-magnesium halogenide complex formed. The original method was improved by adding ethanol to the reaction mixture before filtration of the magnesium salt. The solution was evaporated under reduced pressure at 40°C, the residue was dissolved, in $CHCl_3$, and dried with Na_2SO_4. The solvent was evaporated and the product distilled under reduced pressure or crystallized to give pure dialkylphosphine oxide.

$Et_2P(O)H$, yield: 68%, bp. 48°C/0.4 Torr, lit.[9] bp. 53–55°C/0.5 Torr *n*-$Pr_2P(O)H$, yield: 64%, bp-75°C/0.5 Torr, lit.[10] bp. 71–72°C/1.5 Torr.

n-$Bu_2P(O)H$, yield: 75%, bp. 80°C/0.6 Torr, mp. 54–57°C (from petroleum). lit.[11] 55–58°C (from petroleum).

n-$Octyl_2P(O)H$, yield: 81%, mp. 86°C (from petroleum). Lit.[12] 85°C (from *n*-hexane).

$(CH_2{=}CHCH_2)_2P(O)H$ was synthesised using ethyl ether as solvent for the Grignard synthesis[13] instead of THF. Yield: 37%, bp. 70°C/0.6 Torr, m.p. 35–37°C (from petroleum). $C_6H_{11}PO$ Calc: C, 55.38; H, 8.51; P, 23.80. (130.1) Found: C, 55.21; H, 8.45; P, 37.75. ^{31}P-NMR (Spectrum in C_6H_6): $\delta = 33.8$ p.p.m. ^1H-NMR (in $CDCl_3$, 80 MHz): $\delta = 2.75$ p.p.m. (m, 4 H, PCH_2, $^2J_{PH} = 16.1$ Hz, $^3J_{HPH} = 3.2$ Hz, $^3J_{HH} = 7.3$ Hz), $\delta = 5.10$–6.00 p.p.m. (m, 6 H, ABC system of $H_2C{=}CH$). $\delta = 6.80$ p.p.m (d quintet, 1 H, PH, $^1J_{PH} = 465$ Hz, $^3J_{HPH} = 3.2$ Hz) IR (spectrum in $CHCl_3$) v = 1150 (P=O), 1640 (C=C), 2330 PP—H) cm^{-1}.

Rate of disproportionation of $Et_2P(O)H$. The rate of disproportionation was studied by adding 3.15% of $Et_2P(O)Cl$ or Et_2PCl to $Et_2P(O)H$, and follow the development of the ^{31}P-NMR signal of $Et_2P(O)OH$ at 26°C (Figure 1). Similar experiments were done in the presence of 3.15% Na, and 3.15% HCl (Figure 1).

The non-existence of radical reaction was concluded by comparing the rate of disproportionation of a mixture of $Et_2P(O)H$ (0.574 g, 5.4 mM) and $Et_2P(O)Cl$ (0.0247 g, 0.176 mM) in the absence and presence of hydroquinone (0.0065 g, 0.06 mM) at 26°C. The rates were found to be identical.

TABLE VII

Time dependent molar ratios of reactant and products in the reaction between $R_2P(O)H$ and CCl_4 in benzene at 20°C

COMPOUND	R	Time in hour 1	2	8	24	48	72	120	360
$R_2P(O)H$ (1)	*n*-propyl								
	n-butyl								
	n-octyl					0.39	0.18	0.0	
	allyl					0.70		0.45	0.0
$R_2P(O)OH$ (2)	*n*-propyl	0.15		0.16				0.20	
	n-butyl		0.49		0.40			0.18	
	n-octyl					0.25	0.25	0.25	
	allyl					0.12		0.30	0.43
$R_2P(O)Cl$ (3)	*n*-propyl	0.07		0.12				0.26	
	n-butyl		0.04		0.14			0.43	
	n-octyl					0.06	0.15	0.32	
	allyl					0.00		0.04	0.20
R_2PCl (4)	*n*-propyl	0.05		0.04				0.00	
	n-butyl		0.16		0.15			0.00	
	n-octyl					0.05	0.07	0.00	
	allyl					0.0		0.0	0.0
$(R_2PO)_2O$ (5)	*n*-propyl	0.36		0.32				0.15	
	n-butyl		0.11		0.11			0.11	
	n-octyl					0.08	0.10	0.10	
	allyl					0.13		0.13	0.15
R_2PCCl_3 (6)	*n*-propyl	0.11		0.07				0.00	
	n-butyl		0.16		0.07			0.00	
	n-octyl								
	alkyl								
$R_2P(O)CHCl_2$ (7)	*n*-propyl	0.26		0.29				0.39	
	n-butyl		0.04		0.13			0.28	
	n-octyl					0.17	0.25	0.33	
	allyl					0.05		0.08	0.22

Reaction between $Et_2P(O)H$ *and* CCl_4. $Et_2P(O)H(I)$ (5.3 g, 0.05 M) was added dropwise with stirring to a solution of CCl_4 (0.8 g, 0.052 M) in benzene (10 ml) at 20°C. Stirring was continued for 0.5 h at 20°C, and then kept at 20°C for 66 h. During this period samples were taken at different time intervals for qualitative and quantitative analysis of products, using ^{31}P-NMR, and MS analysis. The analysis of the various products is recorded in Table I. The time dependent molar ratios of the products, based on integrated ^{31}P-NMR signals, are recorded in Table II. After the reaction was finished a sample of the reaction mixture (0.01 M based on $Et_2P(O)H$) was evaporated at 30°C/20 Torr. 3 ml of a saturated solution of $NaHCO_3$ was added, and the solution extracted with $CHCl_3$ (3 × 2 ml). The combined $CHCl_3$ extract was dried over $MgSO_4$, evaporated, and gas chromatographed (GLC, 10% OV-101, 180°C). $Et_2P(O)CHCl_2$, yield: 0.48 g (25.4%), m.p. 47–8°C from (petroleum).

$C_5H_{11}POCl_2$ Calc.: C, 31.77; H, 5.86; P, 16.38. (189.0) Found: C, 31.52; H, 5.81; P, 16.25. ^1H-NMR (in $CDCl_3$, TMS) $\delta = 1.2$ ppm, $^3J_{PH} = 16.1$ Hz, $^3J_{HH} = 7.0$ Hz, (6 H from CH_3), $\partial = 1.6$–2.4 ppm (4 H from CH_2) $\partial = 5.95$ ppm $^2J_{PH} = 1.4$ Hz, (1 H from $CHCl_2$). For other spectral data. see Table I.

Reaction between Et_2PH, $Et_2P(O)OH$ *and* CCl_4. CCl_4 (3.2 g, 0.0207 M) was added to a mixture of Et_2PH (0.9 g, 0.01 M) and $Et_2P(O)OH$ (1.22 g, 0.01 M) in benzene(4 ml) at 20°C. The reaction mixture was kept at 20°C for 66 h. During this period samples were withdrawn and analysed qualitatively and quantitatively. The time dependent molar ratios of the products are recorded in Table III.

Reaction between ET_2PCCl_3 *and* $Et_2P(O)OH$. $Et_2P(O)OH$ (2.44 g, 0.02 M) was added to a solution of Et_2PCCl_3 (4.14 g, 0.02 M) in CH_2Cl_2 (10 ml) at 20°C. The spectroscopic examination of the solution after 24 h showed the product composition recorded in Table IV. Working up of the reaction mixture gave 0.98 g (25.9%) of $Et_2P(O)CHCl_2$, m.p. 47–48°C.

TABLE VIII

Spectral data of dialkyldichloromethylphosphine oxide

$R_2P(O)CHCl_2$ *R* Molecular formula[a]	^{31}P NMR Solvent $CHCl_3$ δ [ppm]	^1H NMR (Solvent, 80 MHz) δ ($-C\underline{H}Cl_2$) [ppm], $^2J_{PH}$ [Hz]	IR μ (P=O) [cm^{-1}]	M.S. m/e (rel. int. %)
Et ($C_5H_{11}Cl_2OP$) (189.0)	55.2	($CDCl_3$), 5.95, 1.4	(nujol), 1180	188, 190 (M^+, 2.6, 1.5); 105 (100); 77.0 (36.9); 49.0 (14.2), 29.0 (11).
n-Pr ($C_7H_{15}Cl_2OP$) (217.0)	52.5	($CDCl_3$), 5.90, 1.3	KBr, 1170	216, 218 (M^+, 5.2, 4.5); 174, 176 (11.0, 7.3); 133 (100).
Allyl ($C_7H_{11}Cl_2OP$) (213.0)	42.2	(C_6D_6), 6.15, 1.0	(neat), 1175	212, 214 (M^+, 4.1, 2.6); 177, 179 (5.6, 1.8); 129 (298), 101 (94.0) 47 (24.1); 41 (100); 39 (48.5)
n-Bu ($C_9H_{19}Cl_2OP$) (245.1)	54.0	($CDCl_3$), 5.88, 1.0	(nujol), 1170	244, 246 (M^+, 6.0, 40.0); 161 (100) 63 (24.2); 55 (23.1).
n-Octyl ($C_{17}H_{35}Cl_2OP$) (357.3)	50.0	($CDCl_3$), 585, 1.1	(neat), 1170	356, 358 (M^+, 3.5, 2.5); 355, 357 [$(M - 1)^+$, 3.4, 2.6]; 321, 323 (4.4, 1.4); 273 (97.8); 55 (77) 43 (66.4); 41 (100).

[a] Satisfactory microanalysis obtained: C ± 0.35, H ± 0.25, P ± 0.3.

Reaction between Et_2PCl, $Et_2P(O)OH$, and CCl_4. $Et_2P(O)OH$ (2.44, g 0.02 M) was added to a stirred solution of Et_2PCl (2.49 g, 0.02 M) and CCl_4 (6.4 g, 0.041 M) in benzene (8 ml) at 20°C. After 66 h the mixture was examined spectroscopically as previously. The molar ratio of the products are recorded in Table IV.

Reaction between Et_2PCl, and $Et_2P(O)OH$. $Et_2P(O)OH$ (2.44 g, 0.02 M) dissolved in $CHCl_3$ (2 ml) was added to a solution of Et_2PCl (2.49 g, 0.02 M) in $CHCl_3$ (8 ml) with stirring at room temperature. After 48 h the reaction mixture was analysed in the usual way. $Et_2PH \cdot HCl$ was identified by its ^{31}P-NMR signal at $\partial = -16.9$ ppm (an authentic specimen in CH_2Cl_2 $\partial = -17.0$ ppm). After neutralizing the mixture the ^{31}P-NMR signal of Et_2PH was found at $\delta = -56$ ppm (lit.[21]. $\delta = -55.5$). Molar ratios of the products are recorded in Table V.

Reaction between $Et_2P(O)H$ and $Et_2P(O)Cl$. $Et_2P(O)H$ (2.12 g, 0.02 M) was added to a stirred solution of $Et_2P(O)Cl$ (2.81 g, 0.02 M) in $CHCl_3$ (10 ml) at 20°C. After 48 h the product composition was determined (Table V).

Dioctylphosphinyl chloride. Dioctylphosphinous acid (2.4 g, 3.92 mM) and PCl_5(0.82g, 3.92 mM) were heated together at 120°C for 1 hour and then distilled; yield: 0.65 g (53.5%); b.p. 135–140°C/0.2 Torr (lit.[14] b.p. 140–3°C/0.03 Torr); m.p. 45–51°C (from petroleum (80–100°C)). ^{31}P-NMR(C_6H_6): $\partial = 71.0$ ppm.

Diallylphosphinyl chloride. Diallylphosphinous acid (1.46 g, 10 mM) was added to a solution of thionyl chloride (1.25 g, 15 mM) in dry ether (15 ml) and the mixture was stirred and refluxed for 0.5 h. The ether was evaporated and the residue distilled under reduced pressure; yield: 1.2 g(72 .9%; b.p. 100°C/2 Torr.

$C_6H_{10}ClOP$ Calc.: C, 43.80; H, 6.12; P, 18.83; (164.5). Found: C, 43.62; H, 6.10; P, 18.65. ^{31}P-NMR (C_6H_6): 57.5 ppm. ^{1}H-NMR (C_6D_6, 80 MHz): $\delta = 2.55$ ppm (4 H,CH_2P., $^2J_{PH} = 7.0$ Hz); $\delta = 4.6$–5.3 ppm (4 H, $CH_2{=}CH$); $\delta = 5.25$–6.15 ppm (2 H, $CH_2{=}CH$).

Diallylphosphinous acid anhydride. Diallylphosphinous acid (0.73 g, 5 mM) was added to a solution of diallylphosphinyl chloride (0.82 g, 5 mM) and triethylamine (0.5 g, 5 mM) in dry ether (10 ml) at 20°C and the mixture was stirred for 2 h. After filtration and evaporation of the solvent, the residue was distilled under reduced pressure; yield: 0.74 g (54%); b.p. 155–7°C/0.5 Torr.

$C_{12}H_{20}P_2O_3$ Calc.: C, 52.55; H, 7.35; P, 22.58; (274.2). Found: C, 52.31; H, 7.15; P, 22.41. ^{31}P-NMR (C_6H_6): 43.2 ppm. H-NMR (C_6D_6, 60 MHz): $\partial = 2.65$ (4 H, CH_2P, $^2J_{PH} = 16.4$ Hz, $^3J_{HH} = 7.0$ Hz); $\delta = 4.7$–5.4 ppm (4 H, $CH_2{=}CH$); $\delta = 5.4$–6.4 ppm (2 H, $CH_2{=}CH$).

Reaction of dialkylphosphine oxide (**1**) *with carbon tetrachloride.*

General synthetic procedure. To a stirred solution of dialkylphospine oxide (0.05 mol in benzene (14 ml for R = Propyl; R = *n*-Butyl; R = Allyl), or in chloroform (35 ml for R = *n*-Octyl), CCl_4 (7 ml, 7.97 g, 0.0518 mol) was added slowly at 20°C in an atmosphere of dry argon. Stirring was continued for 1 hour at 20°C and the solution thereafter kept at 20°C for a time indicated in Table VII. Samples of the mixture were analysed spectroscopically using ^{31}P-NMR. The time dependent product composition is recorded in Table VII. Samples of the reaction mixture (after 1 h for R = Pr, 2 h for R = Bu) was examined by MS confirming the presence of R_2PCCl_3 (R = Pr, Bu): m/c (rel. int., % of M^+) compared with the base peak); Pr_2PCCl_3: 234, 236, 238 (1.8, 2.2, 0.67); Bu_2PCCl_3: 262, 264, 266 (1, 1, 0.4). M.S. were identical with authentic samples.[6] Samples of the reaction mixture (0.02 mole) based on initial dialkyl phosphine oxide) were evaporated after 4 h (R = Pr), 24 h (R = Bu), 120 h (R = Allyl), 72 h (R = *n*-Octyl) at 20°C/5 Torr and distilled under reduced pressure to give three subsequent fractions which according to ^{31}P-NMR spectra contained mainly a) R_2PCl, with following yields and b.p. [°C, Torr]: Pr: 0.39 g, 61–90°/5; Bu: 0.65 g, 45–81°/1 *n*-Octyl, 1.21 g, 82–130°/1, b) $R_2P(O)Cl$, Pr: 0.35 g, 90–126°/5; Allyl: 0.71 g, 52–72°/0.5; Bu: 0.70 g, 81–135°/1; *n*-Octyl: 1.25 g, 131–162°/1 and c) the mixture of $R_2P(O)OH$ (major compound), $[R_2P(O)]_2O$ and $R_2P(O)CHCl_2$, Pr: 2.75 g, 126–155°/5–0.5; Allyl: 2.79 g, 73–151°/0.5; Bu: 3.5 g, 136–165°/1; *n*-Octyl: 3.7 g, 163–224°/1–0.4. Redistillation of fraction a) and b) gave: R_2PCl yield, b.p. [°C]/Torr. (lit. b.p. [°CJ/Torr) Pr: 0.15 g (4.5%). 87–90/5, (84–88/4);[15] Bu: 0.41 g (11%), 75–80°/1, (77–81°/1)[16]; *n*-Octyl: 0.23 g (4%), 130–134°/0.4, (132–5/0.25–0.35)[17] and $R_2P(O)Cl$; Pr: 0.14 g (4%). 58–60°/0.2, (60°/0.2),[18] Bu: 0.42g (10%). 82–84/0.2, (85/0.2);[18] Allyl: 0.52 g (15.8%). 100°/2, (identical with an authentic sample) *n*-Octyl: 0.91 g (14%) 135–140°/0.2, (140–3/0.03).[14] To fraction c) 15 ml 5% aq. sodium hydroxide was added and thereafter extracted with benzene (5 × 15 ml). The benzene solution was dried over anhydrous $MgSO_4$ and evaporated to give crude $R_2P(O)CHCl_2$. After chromatographing (G.L.C., 10% OV-101, 230°C) clean phosphine oxide was obtained; yield: Pr: 0.44 g (10%); Allyl: 0.79 g (15.8%);Bu: 0.38 g (8%); *n*-Octyl: 1.15 g (16%). Physical data of $R_2P(O)CHCl_2$ are recorded in Table VIII.

The alkaline water extract was acidified with concentrated HCl to pH = 1 and extracted with $CHCl_3$ (3 × 10 ml), dried over anhydrous $MgSO_4$ and evaporated to yield dialkylphosphinic acid, (yield, m.p. [°C])); Pr: 1.7 g (56%), 57–8° (from petroleum), (59.5°).[19] Allyl: 1.49 g (51%), oil spectroscopic properties identical with an authentic sample,[6] Bu: 1.61 g (45%), 68–70° (from petroleum), (70–71°);[20] *n*-Octyl: 1.45 g (25%), 82–84° (from petroleum), (85°).[12]

Hydrolysis of dialkylphoshinyl chloride. Dialkylphosphinyl chloride (R = Pr, Allyl, Bu, *n*-Octyl (1 mM) were added to the water-saturated diethyl ether (10 ml), and the mixture evaporated under reduced pressure. The residue was identified as dialkylphosphinic acid by means of spectral properties. Yield: quantitative.

Hydrolysis of dialkylchlorophosphine. Dialkylchlorophosphine (R = Pr, Bu, *n*-Octyl(1 mM) were added to water-saturated diethylether (10 ml) and the mixture evaporated under reduced pressure. The residue was identified by means of spectral properties (Ir, ^1H-NMR as dialkylphosphine oxide. Yield: quantitative.

SYNTHETIC DESCRIPTION FOR DIALKYLDICHLOROMETHYLPHOSPHINE OXIDE:

A. *General procedure for phosphine oxides containing alkyl groups with four or less carbon atoms.* The reactions were carried out in dry argon atmosphere. CCl_4 (12 ml) was added dropwise with stirring to a solution of dialkylphosphine oxide (0.05 mol) in chloroform (30 ml), keeping the temperature at 20–25°C. The reaction solution was refluxed for 3 h and thereafter evaporated under reduced pressure. 20 ml of 15% aq. NaOH was added to the residue and the mixture extracted with benzene (5 × 30 ml). The combined extracts was dried with anhydrous $MgSO_4$. Evaporation of solvent gave the crude product, which was further purified by distillation under reduced pressure or crystallization from petroleum (80°–100°C).

Diethyldichloromethylphosphine oxide; yield: 3.0 g (31.7%); b.p. 135–7°C/0.5 Torr; m.p. 47–8°C.
Dipropyl-dichloromethylphosphine oxide; yield: 3.22 g (29.6%); b.p. 142–5°C/0.5 Torr; m.p. 70 –1°C.
Diallyldichloromethylphosphine oxide; yield: 1.99 g (18.7%); b.p. 145–7°C/0.6 Torr.
Dibutyl-dichloromethylphosphine oxide; yield: 3.62 g (29.6%); b.p. 151–3°C/0.6 Torr; m.p. 48–48.5°C.
Microanalysis and spectral properties are given in Table VIII.

B. *Procedure for phosphine oxide containing long alkyl groups.* Reaction of dioctylphosphine oxide (13.7 g; 0.05 mol) with CCl_4 (7 ml) was carried out as above but using chloroform (35 ml) as solvent. 5 ml water was added to the reaction mixture and the mixture evaporated under reduced pressure. The residue was dissolved in ethanol (350 ml) and passed through Amberlit IRA-400 (basic form in EtOH, 80 ml). The resin was washed with 100 ml of ethanol and the combined eluent evaporated to obtain $(n\text{-octyl})_2P(O)CHCl_2$; yield: 5.57 g (31.2%), (syrup). For microanalysis and spectral data see Table VIII.

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