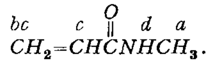
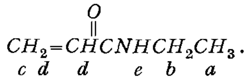

$\overset{bc}{CH_2}=\overset{c}{CH}\overset{\overset{O}{\|}}{C}\overset{d}{NH}\overset{a}{CH_3}$.

B.p. 70–75°/0.3 Torr (contain 9 mol-% $CH_3NHCH_2CH_2CONHCH_3$ (Lit. [14] b.p. 86–87°/3 Torr). ^1H-NMR. (in CCl_4): a) 2.78 and 2.86 (*s*, 2.87H); b) 5.50 ($J_{gem.}$ = 4, J_{trans} = 8, 1H); c) 6.18–6.33 (*m*, 2H); d) 8.33 (br, 0.9H).


$\underset{c}{C}\underset{d}{H_2}=\underset{d}{CH}\overset{\overset{O}{\|}}{C}\underset{e}{NH}\underset{b}{CH_2}\underset{a}{CH_3}$.

B.p. 68–70°/0.033 Torr (Lit. [14] b.p. 85–86°/10 Torr). ^1H-NMR. (in CCl_4): a) 1.15 (*t*, 3.09H); b) 3.25 and 3.37 (2*qu*, 2.03H); c) 5.47 ($J_{gem.}$ = 4.7, J_{trans} = 8, 0.88H); d) 6.18–6.31 (*m*, 2.03H); e) 8.2 (br 0.97H).

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127. Organic Phosphorus Compounds 61

Esterification and Chlorination of Nitrilo-tri(methylenephosphonic acid), $N(CH_2PO_3H_2)_3$, and Hydroxyethylidenediphosphonic Acid, $H_2O_3PC(OH)(CH_3)PO_3H_2$, and the Corresponding Esters[1]

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(13. III. 73)

Summary. Nitrilo-tri(methylenephosphonic acid) and hydroxyethylidenediphosphonic acid are esterified in high yield when treated with excess orthoformic acid ester under reflux. Because of the high temperature necessary to effect esterification a partial isomerization of hydroxyethylidenediphosphonate to the phosphate-phosphonate isomer V takes place. Chlorination of $N(CH_2PO_3H_2)_3$ or a mixture of the ester and the acid with PCl_5 yields tris(chloromethyl)amine, $N(CH_2Cl)_3$. Interaction of $N(CH_2Cl)_3$ and $(EtO)_3P$ yields nitrilo-tri(methylenephosphonate), which on hydrolysis with HCl conc. produces $N(CH_2PO_3H_2)_3$. Chlorination of a mixture of hydroxyethylidene-diphosphonic acid and the corresponding ethyl ester IV which contained the phosphate-phosphonate isomer V gave the products VII to XI. Chlorination of the acid III with PCl_5 gave 4 products, *i.e.* VIII, IX, XI and $Cl_2(O)POP(O)Cl_2$. The ^1H- and ^{31}P-NMR. spectra of the products are discussed.

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[1] Part 60, see [1].

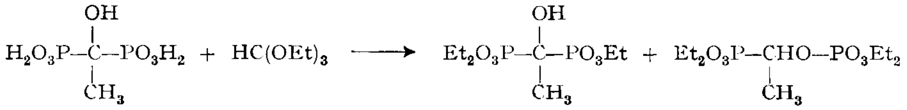
A. Esterification. – The complexing behavior of nitrilo-tri(methylenephosphonic acid), $N(CH_2PO_3H_2)_3$ (I), and hydroxyethylidenediphosphonic acid, $H_2O_3PC(OH)(CH_3)PO_3H_2$ (III), both commercial products, have been studied extensively (for a review see [2]), but little is known about the chemistry of these acids. It therefore seemed of interest to study the esterification and chlorination of these acids.

Esterification of I with orthoformic acid ethyl ester produced the corresponding nitrilo-tri(methylenephosphonate) (II) in quantitative yield:

$$\underset{\text{I}}{N(CH_2PO_3H_2)_3} + 6\,HC(OEt)_3 \longrightarrow \underset{\text{II}}{N(CH_2PO_3Et_2)_3} + 6\,EtOH + 6\,HCO_2Et$$

This ester was obtained previously in a *Mannich* type reaction from diethylphosphite, NH_3 and formaldehyde in 19% yield [3].

The diphosphonic acid III also was esterified in high yield to the ester IV with orthoformic acid ester, but this ester isomerized partially to the isomeric phosphate-phosphonate ester V at the temperature necessary (80–140°) to effect esterification of III. Isomerization of IV to V in the presence of a base has been described in the literature [4], and esterification with orthoformic acid has been used for carboxylic acids [5], benzenephosphonic acid [6], hypophosphorus acid [7], polyphosphonic acids [8], and haloethene-1,2-diphosphonic acids [9].



$$H_2O_3P\text{–}\underset{CH_3}{\overset{OH}{C}}\text{–}PO_3H_2 + HC(OEt)_3 \longrightarrow Et_2O_3P\text{–}\underset{CH_3}{\overset{OH}{C}}\text{–}PO_3Et + Et_2O_3P\text{–}\underset{CH_3}{C}HO\text{–}PO_3Et_2$$

III IV V

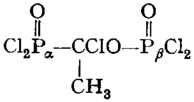
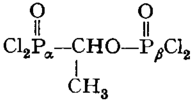
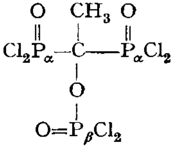
B. Chlorination. – Initially for chlorinating the acids I and III a method was adapted which was previously developed by us for chlorinating alkylene diphosphonates [10]. When a mixture of the acid I and the ester II was heated until homogeneous and then treated with PCl_5 in the presence of $POCl_3$ the only product isolated was tris(chloromethyl)amine, $N(CH_2Cl)_3$ (VI) in 14.6% yield. Much tarry material remained in the reaction flask. This is one of the rare cases where a P–C bond is broken during chlorination with PCl_5 (for other cases see [11], [12]):

$$\underset{\text{I}}{N(CH_2PO_3H_2)_3} + \underset{\text{II}}{N(CH_2PO_3Et_2)_3} \xrightarrow{PCl_5} \underset{\text{VI}}{N(CH_2Cl)_3} + POCl_3 + EtCl + HCl$$

In a related reaction, *i.e.*, chlorination of aminomethanesulfonic acid or nitrilo-tri(methylene sodium sulfonate), $N(CH_2SO_3Na)_3$, with PCl_5 also tris(chloromethyl)-amine (VI) was formed [13].

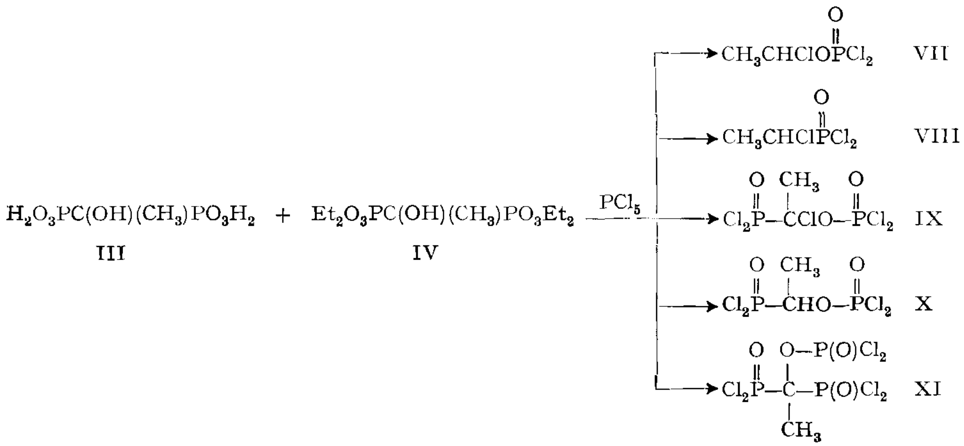
Our sample of $N(CH_2Cl)_3$ was identical in every respect with a sample prepared according to literature methods [13], [14]. Subsequently it was found that chlorination of the acid I with PCl_5 also yielded the amine VI when $POCl_3$ was used as solvent. But no reaction was observed when the acid I was treated with excess $SOCl_2$ under reflux.

Table. *Spectroscopic data of the chlorination products of the acid III and the esters IV and V*

	Compound	^{31}P-chem. shift (in $CHCl_3$) (in ppm)	coupl. const. (in Hz)	^1H-chem. shifts (in $CDCl_3$) in ppm	Lit.
VII	 $CH_3CHClO\overset{O}{\overset{\|}{P}}Cl_2$	-5.5	$J_{POCH} = 10$ $J_{POCCH} = 1$	CH_3 1.95 (2*d*, $J_{HH} = 5.5$, $J_{PCCH} = 1$) CHCl 6.43 (2*qu*, $J_{HH} = 5.5$, $J_{PCH} = 10.5$)	
VIII	 $CH_3CHCl\overset{O}{\overset{\|}{P}}Cl_2$	-46	$J_{PCH} = 2$ $J_{PCCH} = 25$	CH_3 1.87 (2*d*, $J_{HH} = 7$, $J_{PCCH} = 24.8$) CHCl 4.5 (2*q*, $J_{HH} = 7$, $J_{PCH} = 2$)	[12]
IX	 $Cl_2\overset{O}{\overset{\|}{P}}_\alpha-\underset{CH_3}{\underset{\|}{C}}ClO-\overset{O}{\overset{\|}{P}}_\beta Cl_2$	P_α −36.5 P_β −2.0	$J_{P_\alpha CH} = 19.3$ $J_{P_\alpha P_\beta} = 58.2$	CH_3 (in CCl_4) 2.55 (*d*, $J_{P_\alpha CCH} = 19$, small impurity at 4.33 (*d*, $J = 8$)	
X	 $Cl_2\overset{O}{\overset{\|}{P}}_\alpha-\underset{CH_3}{\underset{\|}{C}}HO-\overset{O}{\overset{\|}{P}}_\beta Cl_2$	P_α −41 P_β −7.5	$J_{P_\alpha CH_3} = 24.7$ $J_{P_\beta OCH} = 14.3$ $J_{P_\alpha P_\beta} = 45.5$	CH_3 1.9 (2*d*, $J_{HH} = 7$, $J_{P_\alpha CCH} = 24.3$) CH 5.45 (2*q*, $J_{HH} = 7$, $J_{P_\beta OCH} = 13.5$)	
XI	 $Cl_2\overset{O}{\overset{\|}{P}}_\alpha-\overset{CH_3}{\overset{\|}{\underset{O=P_\beta Cl_2}{\underset{\|}{\underset{O}{\underset{\|}{C}}}}}}-\overset{O}{\overset{\|}{P}}_\alpha Cl_2$	P_α −33.5 P_β −3.2	$J_{P_\alpha CH_3} = 23.2$ $J_{P_\beta CH_3} = 0.8$ $J_{P_\alpha P_\beta} = 20.3$	CH_3 2.6 (2*t*, $J_{P_\alpha P_\alpha CH_3} = 22.6$; $J_{P_\beta CH_3} = 0.82$)	

Hydroxyethylidenediphosphonic acid (III) was also not chlorinated when treated with $SOCl_2$. It was only dehydrated to give the anhydrous acid III of m.p. 190–195° (III. H_2O: m.p. 104–105°).

Therefore a mixture of the acid III and the ester IV was heated until homogeneous, then dissolved in $POCl_3$ and treated with PCl_5 according to:



$$\underset{\text{III}}{H_2O_3PC(OH)(CH_3)PO_3H_2} + \underset{\text{IV}}{Et_2O_3PC(OH)(CH_3)PO_3Et_2} \xrightarrow{PCl_5} \begin{cases} CH_3CHClO\overset{O}{\overset{\|}{P}}Cl_2 & \text{VII} \\ CH_3CHCl\overset{O}{\overset{\|}{P}}Cl_2 & \text{VIII} \\ Cl_2\overset{O}{\overset{\|}{P}}{-}\overset{CH_3}{\overset{|}{C}}ClO{-}\overset{O}{\overset{\|}{P}}Cl_2 & \text{IX} \\ Cl_2\overset{O}{\overset{\|}{P}}{-}\overset{CH_3}{\overset{|}{C}}HO{-}\overset{O}{\overset{\|}{P}}Cl_2 & \text{X} \\ Cl_2\overset{O}{\overset{\|}{P}}{-}\underset{CH_3}{\underset{|}{\overset{O-P(O)Cl_2}{\overset{|}{C}}}}{-}P(O)Cl_2 & \text{XI} \end{cases}$$

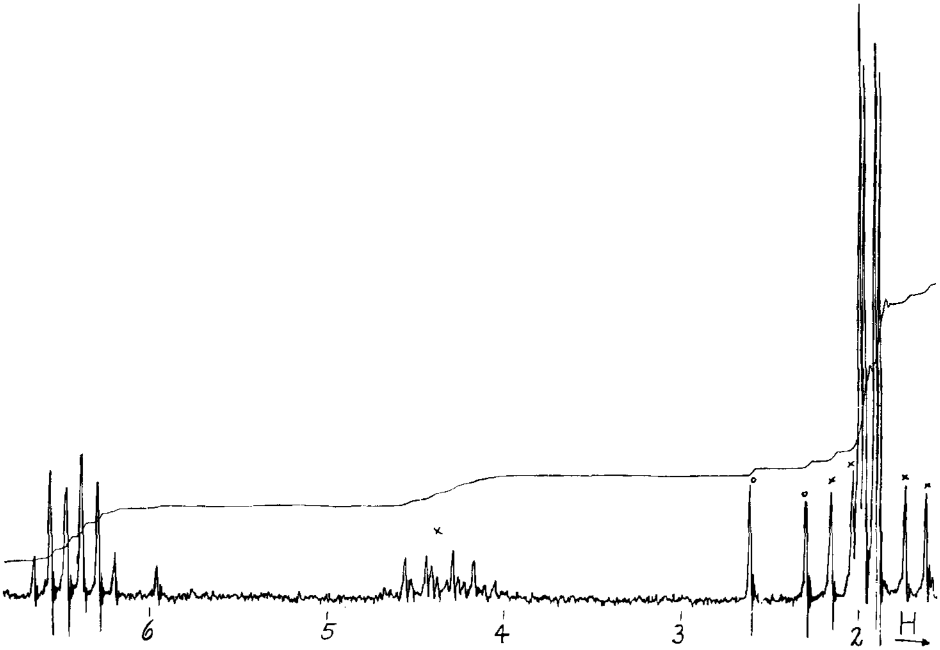
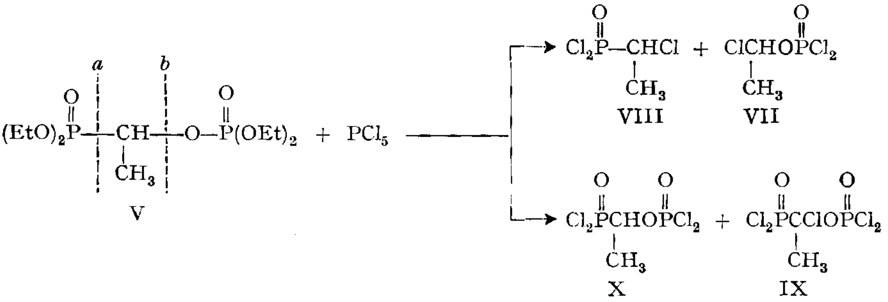


Fig. 1. ^1H-*NMR. spectrum of* $CH_3CHClO\overset{O}{\overset{\|}{P}}Cl_2$ *containing* $CH_3CHCl\overset{O}{\overset{\|}{P}}Cl_2$ (*X*) *and* $Cl_2\overset{O}{\overset{\|}{P}}{-}\overset{CH_3}{\overset{|}{C}}ClO{-}\overset{O}{\overset{\|}{P}}Cl_2$(*O*)

Work-up of the reaction mixture resulted in the isolation of the products VII to XI. Obviously the products VII to X arose from chlorination with PCl_5 of the phosphate-phosphonate isomer V, which was contained in the crude ester IV in an amount of 10% and which was probably formed in even larger quantity during the homogenization process, according to the following equations:



In a previous study of the chlorination of V only product VIII was isolated [4]. The formation of VII must again be ascribed to a P–C bond cleavage (in V at *a*). It would seem that cleavage of V at *a* or *b* occurs with about the same ease. The

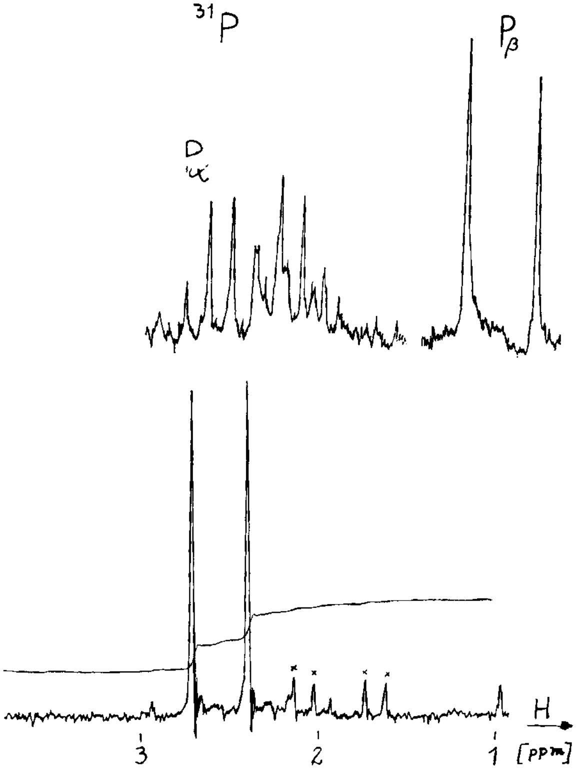
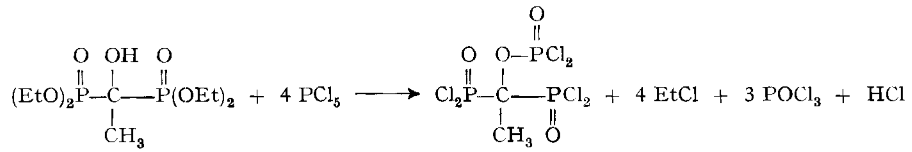


Fig. 2. *¹H- and ³¹P-NMR. spectra of* $Cl_2\overset{O}{\overset{\|}{P}}_\alpha–\underset{CH_3}{\overset{}{C}}ClO–\overset{O}{\overset{\|}{P}}_\beta Cl_2$ *containing* $CH_3CHCl\overset{O}{\overset{\|}{P}}Cl_2$ (*X*)

isolation of IX and X was unexpected. In these products the bridging group was not split. In IX a chlorination of the CH group took place in preference to a cleavage reaction at *a* or *b* in V.

The expected product from the chlorination of the ester IV with PCl_5, *i.e.*, chloroethylidene-1,1-bis(phosphonic dichloride), $Cl_2(O)P-CCl(CH_3)-P(O)Cl_2$ was not obtained. Instead the C–OH group was esterified by $POCl_3$ and 1-phosphoryl-ethylidene-1,1-bis(phosphonic dichloride) XI was isolated:



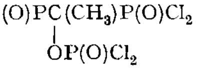
$$(EtO)_2\overset{\overset{O}{\|}}{P}-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-\overset{\overset{O}{\|}}{P}(OEt)_2 + 4\,PCl_5 \longrightarrow Cl_2\overset{\overset{O}{\|}}{P}-\underset{\underset{CH_3}{|}}{\overset{\overset{O-\overset{\overset{O}{\|}}{P}Cl_2}{|}}{C}}-\underset{\underset{O}{\|}}{P}Cl_2 + 4\,EtCl + 3\,POCl_3 + HCl$$

IV XI

Chlorination of the acid III with PCl_5 in $POCl_3$ as solvent gave 4 products *i.e.*,

$CH_3CHClP(O)Cl_2$ (VIII), $Cl_2(O)PCCl(CH_3)OP(O)Cl_2$ (IX),

$Cl_2(O)POP(O)Cl_2$ (XII), and as the main product



$$Cl_2(O)P\underset{\underset{OP(O)Cl_2}{|}}{C}(CH_3)P(O)Cl_2$$

(XI)

Again 1-chloroethylidene-bis(phosphonic dichloride) was not formed. The isolation of VIII and in particular of IX indicates that here also an isomerization reaction occurred. At what stage this isomerization took place is not clear yet. But it is very likely that this isomerization took place before the formation of XI, because it has

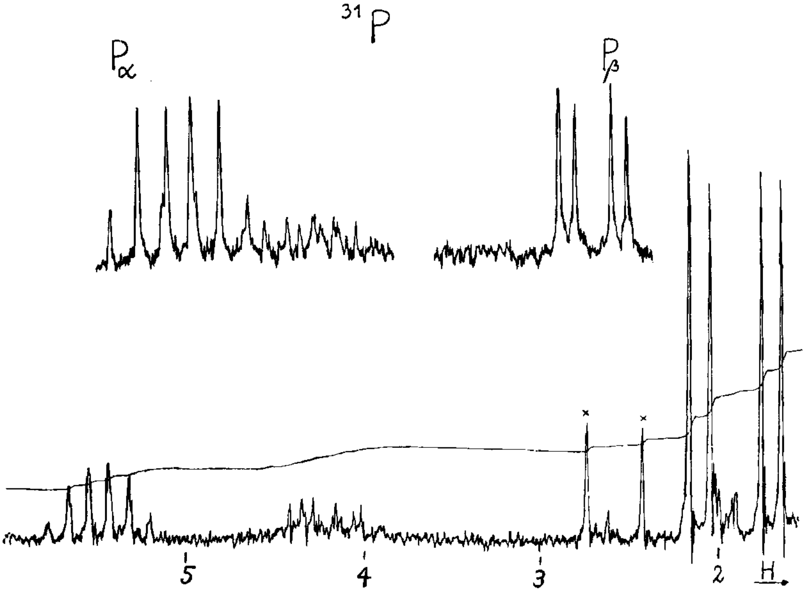
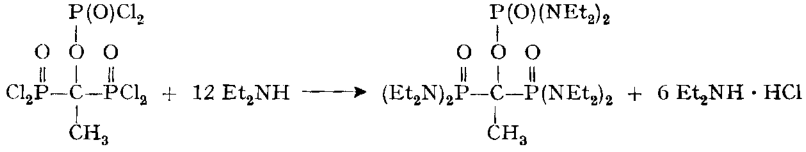


Fig. 3. *^{1}H- and ^{31}P-NMR. spectra of* $Cl_2\overset{\overset{O}{\|}}{P_\alpha}-\overset{\overset{CH_3}{|}}{C}HO-\overset{\overset{O}{\|}}{P_\beta}Cl_2$ *containing* $Cl_2\overset{\overset{O}{\|}}{P}-\overset{\overset{CH_3}{|}}{C}ClO-\overset{\overset{O}{\|}}{P}Cl_2$ (*X*)

been observed that compound XI distills undecomposed at reduced pressure. Furthermore treatment of XI with PCl_5 in refluxing CCl_4 solution results in no reaction. XI was recovered unchanged. XI was also not cleaved when heated with PCl_5 in a bomb tube to 140°.

Interaction of the hexachloride XI and excess diethylamine in ether replaced all the chlorine atoms by diethylamino groups and gave XIII:



$$\mathrm{Cl_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}-\underset{\mathrm{CH_3}}{\underset{|}{\overset{\mathrm{P(O)Cl_2}}{\overset{|}{\overset{\mathrm{O}}{\overset{|}{\mathrm{C}}}}}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}\mathrm{Cl_2} + 12\,\mathrm{Et_2NH} \longrightarrow \mathrm{(Et_2N)_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}-\underset{\mathrm{CH_3}}{\underset{|}{\overset{\mathrm{P(O)(NEt_2)_2}}{\overset{|}{\overset{\mathrm{O}}{\overset{|}{\mathrm{C}}}}}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}\mathrm{(NEt_2)_2} + 6\,\mathrm{Et_2NH \cdot HCl}$$

XI XIII

C. Spectroscopic Data. – The ^1H- and ^{31}P-NMR. data of the chlorination products of the acid III and the esters IV and V are summarized in the table and the

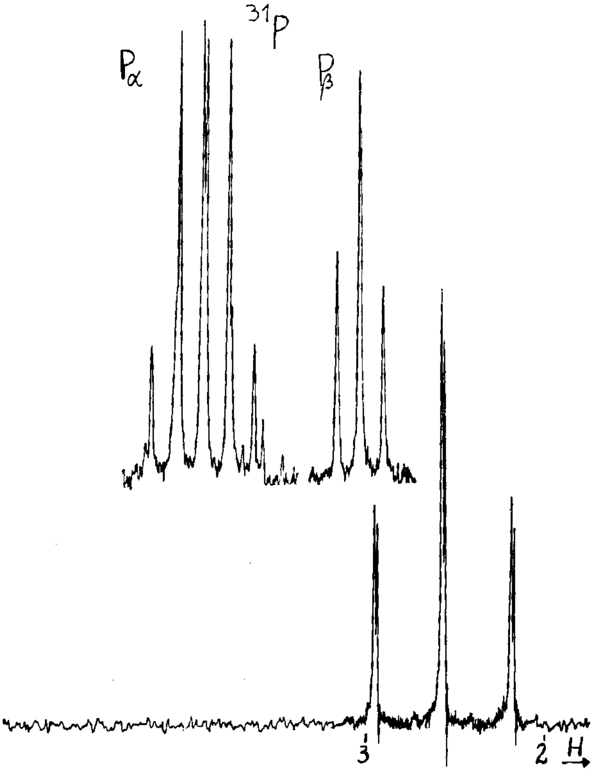
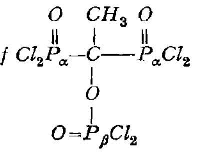
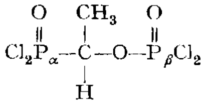


Fig. 4. *^1H- and ^{31}P NMR. spectra of*



$$Cl_2\overset{O}{\overset{\|}{P_\alpha}}-\underset{O=P_\beta Cl_2}{\underset{|}{\underset{O}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}}}-\overset{O}{\overset{\|}{P_\alpha}}Cl_2$$

individual spectra are given in the Fig. 1 to 4. Analysis of the spectra for the compounds VII and VIII is straight forward. Of particular interest are the ^{31}P-NMR. spectra of IX to XI. When in the compound:



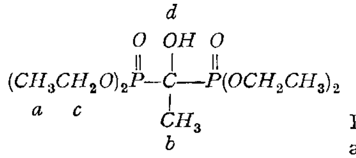
$$\mathrm{Cl_2P_\alpha(O){-}C(CH_3)(H){-}O{-}P_\beta(O)Cl_2}$$

the H on the bridging C atom is replaced by the more electronegative groups Cl and finally by the phosphoryl group $P(O)Cl_2$ the shift of P_α moves to higher fields from -41 to -36.5 to -33.5 ppm, respectively, which indicates that P_α becomes more and more shielded. A similar trend has been observed previously in the series of allyl- and α- and β-chlorosubstituted alkylphosphonates and alkylenediphosphonates with varying chain length in the bridging group [16]. Furthermore the coupling constant $P_\alpha P_\beta$ increases when going from H to the Cl substituent from 45.5 to 58.2 Hz. In the case of the phosphoryl-substituent the coupling constant $P_\alpha P_\beta$ of 20.3 Hz cannot be directly compared because we have here a case of virtual coupling.

Experimental Part

(with Miss *H. Benz* and Mr. *H. P. Dettling*)[2])

1. *$N[CH_2P(O)(OEt)_2]_3$* (II). A mixture of 14.8 g (0.05 mol) of $N(CH_2PO_3H_2)_3$ (I), and 88.8 g (0.6 mol) of $HC(OEt)_3$ is refluxed for two h. Then excess ester and alcohol is distilled and the residue kept at 100° under reduced pressure to remove all volatile products. Crude II, a colorless oil is obtained in quantitative yield. The ^1H-NMR. spectrum was the same as that of a distilled sample, b.p. ~160°/0.3–0.2 Torr (lit. [3] b.p. 202–204°/0.8 Torr); ^{31}P -23 ppm (neat) (lit. [15] -22.6 ppm). ^1H-NMR. (in CCl_4): CH_3 1.30 (*t*, $J_{HH} = 7$, 18.3H); NCH_2 3.22 (br *d*, $J_{PCH} = 11$, 5.4H); OCH_2 4.07 (2 *qu*, $J_{HH} = 7$, $J_{POCH} = 8$, 12.3H).

2. 

$$(CH_3CH_2O)_2P(O){-}C(OH)(CH_3){-}P(O)(OCH_2CH_3)_2$$

(IV). From 51.5 g (0.25 mol) of $H_2O_3PC(OH)(CH_3)PO_3H_2$ (III) and 370 g (2.5 mol) of $HC(EOt)_3$ as in 1. After removing all the volatile products a colorless liquid is obtained which according to the ^1H-NMR. spectrum consists of 90 mol-% IV and 10 mol-% isomer V, $Et_2O_3PCH(CH_3)O{-}PO_3Et_2$, (lit. [4] m.p. of IV 38–38.9°).

IV.: ^1H-NMR. (in $CDCl_3$): a) 1.3 (*t*, $J_{HH} = 7.5$); b) 1.54 (*t*, $J_{PPCH_3} = 15.5$); a+b 15.4H; c) 4.15 (*m*); d) 4.10 (*s*); c+d = 8.61H. ^{31}P -20 ppm (neat) (lit. [4] -20.8 ppm, $J_{PPCH_3} = 16$).

V. ^1H-NMR. (in $CDCl_3$): b) 1.6 (*d*, $J_{HH} = 7.5$ complex); other peaks are the same as in IV. ^{31}P -20 and $+0.5$ ppm (lit. [4] -21 and $+1$ ppm).

In an attempt to distill part of the product, b.p. 118–142°/2.2–1.2 Torr, not only isomerization of IV to V was observed but also a decomposition reaction occurred since the ^{31}P-NMR. spectrum showed now 6 peaks at -21 (~50%); -17 (~10%); -14 (~5%); -1 (~5%); $+1.5$ (~25%) and $+6$ (~5%) [ppm].

B. Chlorination. – 3. Chlorination of a mixture of $N(CH_2PO_3Et_2)_3$ (II) and $N(CH_2PO_3H_2)_3$ (I) with PCl_5: A mixture of 116.7 g of II and 66.7 g (0.25 mol) of I is heated until homogeneous and then treated with 625 g (3 mol) of PCl_5 at 60°. Since the mixture became solid, 100 ml of $POCl_3$

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[2]) Microanalysis were performed by *W. Manser*, ETH, Zürich. The NMR. spectra were run on a *Varian* HA 60 IL instrument using H_3PO_4 (for ^{31}P) and TMS (for ^1H) as reference. Shifts are given in ppm and coupling constants in Hz.

were added and then addition of PCl_5 continued for 2.5 h. $POCl_3$ was distilled, the residue refluxed with 1000 ml C_6H_6, filtered, treated with carbon black, filtered and the filtrate evaporated to give an oil which crystallized after standing at room temperature, 11.9 g (= 14.6%). Sublimation gave pure $N(CH_2Cl)_3$ (VI) of m.p. 89–91° (lit. [13] m.p. 90–92°; [14] 93°). ^1H-NMR. (in CCl_4): CH_2 5.05 (*s*) (lit. [14] 4.9 (in CH_2Cl_2). The product was identical with an authentic sample prepared from hexamethylenetetramine and PCl_5 [14].

4. *Chlorination of* $N(CH_2PO_3H_2)_3$ *(I) with* PCl_5 *to give* $N(CH_2Cl_3)$ *(VI)*. The amine VI is also formed when the acid I (0.1 mol) is treated with 1.2 mol of PCl_5 at 100°. Thereby HCl and $POCl_3$ is formed. The mixture is refluxed for 3 h, then $POCl_3$ distilled and the residue extracted with benzene, filtered and the filtrate evaporated. The residue consists of slightly yellow crystals and a liquid. The crystals are filtered and dried under vacuum. Their ^1H-NMR. sepctrum was identical with that of $N(CH_2Cl)_3$.

5. *Preparation of* $N(CH_2PO_3Et_2)_3$ *(II) from the amine VI and* $P(OEt)_3$. To 8.9 g (0.0518 mol) of $N(CH_2Cl)_3$ is slowly added 54.5 g (0.328 mol) of $(EtO)_3P$ over a period of 40 min. A vigorous exothermic reaction ensues and the temperature rises to 92°. The mixture is refluxed for 4 h and all volatile material removed at 80° under high vacuum. According to the ^1H-NMR. spectrum the residue (20.8 g = 81.5%), a slightly yellow oil, is pure II. A part is distilled, b.p. 161–182°/0.25 Torr. ^1H-NMR. (in CD_3OD): CH_3 1.32 (*t*, 18H); PCH_2 3.37 (*d*, J_{PCH} = 10, 6H); OCH_2 4.15 (2 *qu*, 12H).

6. *Hydrolysis of II to give* $N(CH_2PO_3H_2)_3$ *(I)*. A mixture of 20.8 g of II and 60 ml of HCl conc. is refluxed for 6 h, evaporated under reduced pressure and since the ^1H-NMR. spectrum showed the presence of ethoxy-groups, the residue is again refluxed for 7.5 h with 50 ml of HCl conc. After evaporation the last traces of water are removed by azeotropic distillation with benzene. A viscous slightly yellow mass is obtained which crystallizes after standing for some time to give 13.3 g (= 100%) I, m.p. 195–210° (dec.). ^{31}P – 9 ppm (in H_2O) (lit. [15] – 8 ppm, dec. 210–215°). ^1H-NMR. (in D_2O): CH_2 4.32 (*d*, J_{PCH} = 12.5, 2H); OH 5.83 (*s*, 6H).

7. *Chlorination of a mixture of the acid III,* $H_2O_3PC(OH)CH_3PO_3H_2$ *and the ester IV with* PCl_5. A mixture of 79.5 g (0.25 mol) of IV containing 25 mol-% V and 51.5 g (0.25 mol) of acid III is heated until homogeneous. Since this mixture solidified on cooling to 0°, 50 ml of $POCl_3$ are added and then with stirring 520 g of PCl_5 (2.5 mol) over a period of 3 h at 0°. The mixture is refluxed for 1 h and $POCl_3$ distilled at reduced pressure. The residue, a brown oil, did not crystallize when dissolved in petrol ether or benzene. The benzene solution was refluxed with carbon black, filtered over celite and evaporated to give 63.4 g crude product, 27 g of which were fractionated. The following fractions were obtained: a) b.p. 38–102°/3.3–3.6 Torr, 1 g containing mainly $CH_3CHClOP(O)Cl_2$ (VII) (80 mol-%) and some $CH_3CHClP(O)Cl_2$ (VIII) (20 mol-%) and another unidentified impurity. Found C 15.68 H 2.68 Cl 46.34 P 13.17%

b) b.p. 102–127°/3.5 Torr, 1.8 g consisting mainly of $Cl_2(O)PCH(CH_3)OP(O)Cl_2$ (X) (85 mol-%), some $Cl_2(O)P{-}C(CH_3)[OP(O)Cl_2]P(O)Cl_2$ (XI, 11 mol-%) and $Cl_2(O)P{-}CCl(CH_3)O{-}P(O)Cl_2$ (IX) and some other impurity; c) b.p. 127–153°/3.6–40 Torr, 10.4 g consisting of 80 mol-% XI and 20 mol-% X; d) b.p. 120–133°/0.5–0.6 Torr, 3.0 g pure XI, crystallizes completely and melts after recrystallization from ether at 51–52°.

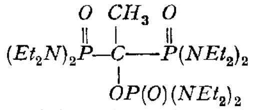
$C_2H_3Cl_6O_4P_3$	Calc.	C 6.05	H 0.76	Cl 53.62	P 23.42%
(396.7)	Found	,, 6.64	,, 1.11	,, 53.00	,, 22.59%

8. *Chlorination of the acid* $H_2O_3P{-}C(OH)CH_3{-}PO_3H_2$ *(III) with* PCl_5. To 30.9 g (0.15 mol) of III is added 137.3 g (0.66 mol) of PCl_5 and the mixture stirred at 100° for 3 h. Since only little $POCl_3$ and HCl is formed, 50 ml $POCl_3$ are added and heating is continued for 2 h under reflux. Then $POCl_3$ is distilled and the residue dissolved in 300 ml hot benzene, filtered and evaporated to give crude XI (14.9 g = 25.2%) which contained a hydrogen containing impurity and $Cl_2(O)P{-}{-}O{-}P(O)Cl_2$ (XI) (^{31}P + 9 ppm). Fractionation gives: a) b.p. 50–70°/0.15 Torr, 0.8 g containing VIII, IX and XII; b) b.p. 70–108°/0.15 Torr, 1.8 g consisting of 80 mol-% IX and 20 mol-% XII; c) b.p. 108–143°/0.15 Torr, 8.5 g nearly pure XI.

Fraction b was 'Kugelrohr' distilled to give nearly pure IX, $Cl_2(O)P{-}CCl(CH_3)O{-}P(O)Cl_2$, b.p. 80°/0.05 Torr.

$C_2H_3Cl_5O_3P_2$	Calc.	C 7.65	H 0.96	Cl 56.41	P 19.71%
(314.3)	Found	,, 7.17	,, 0.89	,, 55.71	,, 18.27%

9. *Reaction of acid III with $SOCl_2$*. On heating 20.6 g (0.1 mol) of III monohydrate (m.p. 104–105°) with 119 g $SOCl_2$ for 10 h under reflux, the anhydrous acid III of m.p. 190–195° was obtained. It readily takes up one mol of water to form the monohydrate which titrates as a tetrabasic acid with inflection points at pH 5.12 (2 eq. Found 116.4, Calc. 112) and pH 9.1 (2 eq. Found 114.2, Calc. 112).

10. 

$$(Et_2N)_2\overset{O}{\overset{\|}{P}}-\underset{\underset{OP(O)(NEt_2)_2}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{O}{\overset{\|}{P}}(NEt_2)_2$$

(XIII). To 2.98 g (0.01 mol) of crystalline XI in 50 ml Et_2O is added 11.6 g of Et_2NH with ice cooling. A white precipitate forms immediately. After 2 h at reflux, $Et_2NH \cdot HCl$ is filtered and the filtrate evaporated and kept under high vacuum to remove all volatile material. As a residue is obtained in low yield XIII, a brownish oil. ^{1}H-NMR. (in $CDCl_3$): CH_3 1.20 (*t*, 36.9H); C–CH_3 2.25 (*t*, $J_{PPCH_3} = 21$, 3.6H); and CH_2 3.15 (*m*, 22.4H).

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128. Chaenorhin, ein macrocyclisches Spermin-Alkaloid[1])

149. Mitteilung über Alkaloide[2])

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(26. III. 73)

Summary. Structure **1** has been elucidated for chaenorhine, an alkaloid isolated from *Chaenorhinum origanifolium* (*Scrophulariaceae*). The key derivative for the structural elucidation is 13,14,21,22-tetrahydro-21,22-*seco*-chaenorhine (**21**). **21** gave upon hydrolysis spermine and 4-hydroxydihydrocinnamic acid characterized as the tetraacetyl derivative **18** and as the dimethyl derivative respectively.

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[1]) Auszugsweise vorgetragen an der Sommerversammlung der Schweizerischen Chemischen Gesellschaft am 17. 10. 1970 in Basel [1].

[2]) 148. Mitt., vgl. [2].