REACTIONS OF DICHLOROTHIOPHOSPHORYLIMIDOPHOSPHORUS TRICHLORIDE WITH NUCLEOPHILIC REAGENTS

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Dichlorothiophosphorylimidophosphorus trichloride, $Cl_3P = NP(S)Cl_2$ (I), can be a valuable intermediate in the synthesis of physiologically active compounds. However, its chemical properties have been studied very little. It is known only that I reacts with sodium phenolate [1] or sodium alcoholate [2] to form triphenyl (diphenoxythiophosphorylimido)phosphate (II) or trialkyl (dialkoxythiophosphorylimido)phosphate, respectively.

We have already improved the method for obtaining I [3]. The present work is a study of its reaction with alcohols, phenol, and secondary amines. By analogy with $Cl_3P = NP(O)Cl_2$, the chemical properties of which were studied in [4], in the reactions of I with nucleophilic reagents we should expect high lability for a Cl at the imidated P atom, and lowered lability for the Cl atoms attached to the thiophosphoryl group.

Using ³¹P NMR, PMR, and IR spectroscopy we studied the structure of the reaction products of I with the above nucleophilic reagents. It is known [5] that for $Cl_3P=NP(O)Cl_2$ the signals with $\delta = -0.1$ and -14.2ppm* correspond to the imidated and the phosphoryl P atoms, respectively. Similarly, in I the signals in the regions of -3.4 and 28.4 ppm belong to the imidated and the thiophosphoryl P atoms, respectively [6]. The imidophosphate II and hexamethyltriamido(tetramethyldiamidothiophosphorylimido)phosphate (III) were synthesized, and their ³¹P NMR spectra were studied.

 $(C_6H_5O)_3P' = NP''(S)(OC_6H_5)_2 (II) [(CH_3)_2N]_3P' = NP''(S)[N(CH_3)_2]_2 (III)$

Imidophosphate II was obtained from triphenyl phosphite and diphenyl azodithiophosphate; its synthesis and constants are given in the experimental part. Compound III was obtained by the method described in [7].

The ³¹P NMR spectrum of II shows signals in the -22.2 and 46.6 ppm regions, which must be assigned to P' and P"; similarly in the NMR spectrum of III the signals in the 20.1 and 60.5 ppm regions correspond to P' and P". The PMR spectrum of III consists of two doublets, at 2.70 and 2.50 ppm, with intensity ratio 3:2, that must be assigned to the CH_3 protons at the imidated and thiophosphoryl atoms, respectively. The values of the chemical shifts of the imidated P atom in $R_nCl_{3-n}P=NP(O)Cl_2$ compounds ($R = OC_6H_5$, NR'_2 ; n = 1, 2) are given in [4].

Compound I reacts easily with alcohols at a 1:1 reagent ratio to form the unstable monoalkoxy derivatives IVa-c, as confirmed by the NMR spectrum of the reaction mixtures; when heated they isomerize to the thiol isomers Va-c:

$$[(RO)Cl_2P'=NP''(S)Cl_2] (IVa-c) (RS)Cl_2P'=NP''(O)Cl_2 (Va-c)$$

where

$$R = CH_3$$
 (a); C_2H_5 (b); C_4H_9 (c).

At 140–150°C, I reacts readily with phenol, and at 1:1 reagent ratio the monophenoxy derivative VI separates in good yield; structure VI' might also correspond to it:

$$(C_{6}H_{5}O)Cl_{2}P = NP(S)Cl_{2} (VI) \qquad Cl_{3}P = NP(S)Cl(OC_{6}H_{5}) \qquad (VI')$$

*The δ value of ³¹P in the weak field is considered positive.

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However, the presence of signals in the -3.5 and 29.8 ppm regions in the PMR spectrum permits VI' to be excluded from consideration. This conclusion is confirmed by the synthesis of phenyl (dichlorothiophosphoryl-imido)dichlorophosphate (VI) by the procedure of [8].

The IR spectra of the preparations obtained by the two methods are identical; the constants are given in Table 1, and the IR and 31 P NMR data in Table 2.

At 150-160°C, I reacts with phenol at 1:2 reagent ratio, to form diphenyl (dichlorothiophosphorylimido)chlorophosphate (VII), the structure of which is confirmed by the characteristic P'and P" signals in the 31 P NMR spectrum in the -12.5 and 31.0 ppm regions.

$$(C_6H_5O)_2ClP' = NP''(S)Cl_2$$
 (VII)
 $(C_6H_5O)_8P = NP(S)Cl_2$ (VIII)

At 1:3 reagent ratio, I reacts with phenol at $170-180^{\circ}$ C, but the reaction products undergo substantial decomposition. The presence of pyridine hydrochloride facilitates the reaction, thanks to which we were able to obtain triphenyl (dichlorothiophosphorylimido)phosphate (VIII) in good yield. In the ³¹P NMR spectrum of VIII the signals in the -25.2 and 31.2 ppm regions are evidence that there are three phenoxy groups at the imidated P, and that a dichlorothiophosphoryl group is present.

In the presence of pyridine hydrochloride (I) at $225-240^{\circ}$ C all the Cl atoms are replaced by phenoxy groups. The structure of phosphate II, which separates in small yield, is confirmed by elemental analysis, ³¹P NMR and IR spectra, and the agreement of the melting point with the data of [1].

The explanation of the order in which phenoxy groups enter I is apparently to be sought in the insignificant change in reactivity of the two P atoms to nucleophilic reagents when one or two phenoxy groups replace Cl atoms at the imidated P; therefore, the replacement of the second or third Cl by phenoxy takes place at the imidated P. We have similarly explained the order in which phenoxy groups enter the pentachloride molecule [4].

Compound I reacts readily with amines. Thus, I and dimethylamine at 1:2 ratio form dimethylamido-(dichlorothiophosphorylimido)dichlorophosphate (IX)

$$[(CH_3)_2N]Cl_2P'=NP''(S)Cl_2$$
 (IX) $Cl_3P=NP(S)Cl[N(CH_3)_2]$ (IX')

The alternate structure, trichloro(dimethylamidochlorothiophosphorylimido)phosphate (IX'), must be rejected on the basis of the ³¹P NMR spectrum; the signals in the 6.4 and 31.0 ppm regions belong to the P' and P" atoms. Additional confirmation is the synthesis of imidophosphate IX from dimethylamido(dichlorophosphorylimido)dichlorophosphate by:

$$[(CH_3)_2N]Cl_2P = NP(O)Cl_2 + P_2S_5 \rightarrow (IX)$$

The constants of the substances thus obtained are given in Table 1; the IR, PMR, and ³⁴P NMR data in Table 2.

Compound I and dimethylamine react at 1:4 ratio to form a substance the elemental composition of which corresponds to the following disubstituted products:

$$\begin{array}{c} [(CH_3)_2N]_2PCl = NP(S)Cl_2 \quad [(CH_3)_2N]Cl_2P = NP(S)Cl[N(CH_3)_2] \\ (X) & (X') \\ Cl_3P = NP(S)[N(CH_3)_2]_2 \\ (X'') \end{array}$$

The ³¹P NMR spectrum consists of four doublets, with δ 21.4 and 31.5 ppm (J_{PNP} = 20.2 Hz) and 7.6 and 58.4 ppm (J_{PNP} = 37.8 Hz). The signals in the 21.4 and 31.5 ppm regions correspond to imidophosphate X, while those in the 7.6 and 58.4 ppm regions must be assigned to imidophosphate X'. The X" structure is inconsistent with the NMR spectrum and the chemical properties of I described above. The X:X' ratio is 3:1, according to NMR. Unfortunately, the individual isomers could not be isolated.

Compound I and dimethylamine react at 1:6 ratio to form the trisubstituted XI, to which one of the following three formulas may be assigned:

R W		Phenoxy	and Dialk	ylami 	ido De	erivative	es of the Thiop	entachlo	bride RI	R'nCl _{2-r}	P = NP(S)R'mC	l2-m
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		В	¥	<i>u</i>	m	Yield,	ьр, °С	20	420	Found/C	alculated,	0/0	Emnirical formula
			;	:		%	(p, mm Hg) mp, °C	ſſ.,	Ъ.	ច	h	ø	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	ច		C ₆ H ₅ O	*-	0	64	148 - 149(0,3)	1,5924	1,5645	_	18,0 18.1	9,8 9.4	C ₆ H ₅ Cl ₄ NOP ₂ S
$ \begin{array}{ ccccccccccccccccccccccccccccccccccc$				4	0	30 *	135 - 138(0, 15)	1,5951	1,5673		17.7	r S	,
$ \begin{array}{lcccccccccccccccccccccccccccccccccccc$	ច		C ₆ H ₅ O	5	0	73	130 - 132(0,1)	1,5948	1,4455	26,6	10,1	8,1	$C_{12}H_{10}Cl_3NO_2P_2S$
$ \begin{array}{lcccccccccccccccccccccccccccccccccccc$	CeH	0	C ₆ H ₅ O	¢1	0	63	169-171 (0,005)	1,5982	1,3644	20,0 15,5		7.0	C ₁₈ H ₁₅ Cl ₂ NO ₃ P ₂ S
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	C ₆ H	°,	C ₆ H ₅ O	21	2	26	96-98	ļ	I	13,5	10,9	6,1	C30H25NO5P2S
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Ũ		(CH ₃) ₂ N	٣	0	29	140-141(0,3)	1.5703	1,2629	48,3	21,2		$C_2H_6Cl_4N_2P_2S$
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$				*1	0	22 *	126 - 129(0,2)	1,5681	1,5676	48,3	21,1 20,7 21,1	<u>11,0</u> 10,9	
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	C	_	(CH ₃) ₂ N	2	4	51	104 - 106(0,005)	1,5439	1,2636	22,2	19,9 19.9		$C_6H_{18}Cl_2N_4P_2S$
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	U		(CH ₃) ₂ N	~	57	50	102 - 104(0,005)	1,5274	1,1685	11,4	2	10,0	$\rm C_8H_{24}CIN_5P_2S$
H3)2N (CH ₃)2N (CH ₃)2N (CH ₃)2N 2 72 135-137(0,2) 1,5242 - 17.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 15.242 1.5242 1.5242 1.57.3 $\frac{17.3}{16.7}$ 0.1 0.1	(CH	[3) 2N	(CH ₃) ₂ N	21	57	76	100 - 101 (0,5) 57 - 58	I	1	11,1	18.5	9,7	$C_{10}H_{30}N_6P_2S$
$ \begin{array}{ c c c c c c c c } \hline \begin{array}{l} \hline \\ \hline $	(C ₂ 1	H5) 2N	$(CH_3)_2N$	53	3	72	135 - 137(0,2)	1,5242	I		17,2	1	$C_{12}H_{34}N_6P_2S$
$ \begin{array}{ c c c c c c c c } (C_{a}H_{5})_{2}N & 1 & 0 & 74 & 145-148(0,3) & 1.5542 & 1.4573 & 43.8 & 19.2 & 10.3 & C_{4}H_{10}Cl_{1}N_{2}P_{2}S \\ \hline 1 & 1 & 0 & 41* & 138-139(0,2) & 1.5557 & 1.4602 & & 19.2 & 10.3 & C_{4}H_{10}Cl_{1}N_{2}P_{2}S \\ \hline 1 & 1 & 0 & 70^{\dagger} & 138-140(0,2) & 1.5543 & 1.4576 & \frac{44.3}{44.0} & \frac{19.2}{19.1} & \frac{10.3}{10.0} & C_{4}H_{10}Cl_{1}N_{2}P_{2}S \\ \hline (C_{a}H_{5})_{2}N & 1 & 1 & 40 & 106-108(0,005) & 1.5369 & 1.2885 & \frac{29.5}{29.7} & \frac{17.3}{17.3} & C_{4}H_{20}Cl_{3}N_{3}P_{2}S \\ \hline \end{array} $	\sim	N	(CH ₃) ₂ N	~1	27	69	180 - 185(0,5)	1	ł		16,9 16,9 16,7	9,1 8,7	C ₁₂ H ₃₂ N ₆ OP ₂ S
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	ប		$(C_2H_5)_2N$		0	74	145-148(0,3)	1,5542	1,4573	43,8	19,2 19,1	10,3 10,0	$C_4H_{10}Cl_4N_2P_2S$
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$					0	41 *	138 - 139(0,2)	1,5557	1,4602		$\frac{19,2}{19,1}$		
$ \begin{array}{ c c c c c c c c } (C_{2}H_{s})_{s}N & 1 & 1 & 4 & 0 \\ \hline & & & & & & & & & & & & & & & & & &$				**1	0	70 +	138 - 140(0,2)	1,5543	1,4576	44,3 44,0	18,8 19,1		
	CI		(C ₂ H ₅) ₂ N	4	4	40 40	106-108(0,005)	1,5369	1,2885	29,5	17,3		C ₆ H ₂₀ Cl ₃ N ₃ P ₂ S

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*Obtained by reaction of P_2S_5 with respective phosphorylimidophosphate, $RCl_2P = NP(O)Cl_2$. [†]Obtained by reaction of the thiopentachloride with diethylaminotrimethylsilane.

1 AD LE 4	. Fuenoxy		A LAILLIU		auves or 1	niopentaci	nioriae Kh		H(2) AN =	m ^{Cl} 2-m	
, amond		È	1	-	IR spectrum	, cm ⁻¹	PMR spect	rum, ppm	³¹ P-{ ¹ H} N	IMR spectrum	ı, ő, ppm
ninon	4	Y.	r	۴	vP==N	vP=S	$\substack{\delta (\mathrm{CH}_3)_2 \mathrm{N} \\ (\mathrm{P} = \mathrm{N})}$	$ \substack{\delta (\mathrm{CH}_3)_2 \mathrm{N} \\ (\mathrm{P} = \mathrm{S}) } $	ôP'	δ₽"	JPNP, HZ
(IVI)	CI	C ₆ H ₅ O	+	0	1320	690	I	I	-3,5	29,8	20,7
			1	*0	1300	690	1	I	-3,7	29,6	31,0
(III)	CI	C ₆ H ₅ O	2	0	1330	690	I	I	-12,5	31,0	30,5
(IIII)	C ₆ H ₅ O	C ₆ H ₅ O	2	0	1330	670	1	1	-25,2	31,2	36,6
(11)	C ₆ H ₅ O	C ₆ H ₅ O	2	2†	1320	690	1	1	-22,2	46,6	68,3
			2	2	1320	. 690	1	1			
(IX)	CI	$(CH_3)_2N$	-	0	1320	680	3,04	ł	6,4	31,6	14,6
			Ļ	*0	1320	680	3,01	I			
(XI)	CI	$(CH_3)_2N$	2	*1	1290	680	2,87	2,79	26,1	60,6	42,7
(XII)	CI	(CH ₃) ₂ N	7	57	1300	670	2,88	2,62	23,7	63,7	41,5
(111)	(CH ₃) ₂ N	$(CH_3)_2N$	5	7	1305	670	2,70	2,50	20,1	60,5	54,9
			73	2†	1305	670	2,71	2,50			
(XV)	cı	$(C_2H_5)_2N$	1	0	1300	680	I	I	2,5	31,0	15,1
			Ŧ	*0	1300	680	I	!	2,4	30,9	15,3
			-	# 0	1300	680	ł	1	I	ļ	I
(XVI)	CI	(C ₂ H ₅) ₂ N	1	7	1305	680	1	1	1,8	53,9	39,1
*Obtained †Reaction ‡Obtained	I from RC products from I a	1 ₂ P=NP(O) of R ₃ P and rd (CH ₃) ₃ Si)Cl ₂ and 1 R' ₂ P(S N(C ₂ H ₅)	l P ₂ S ₅ . ()N ₃ . 2.							

ξ 1 C /S/II CIN Ę RR' CL : 1 - 1 - 1 - 1 ĉ of Thim and Dialkylamido Derivatiyas į TARLE 2. Phenor

$$\begin{array}{c} [(CH_3)_2N]_2ClP = NP(S)Cl[N(CH_3)_2] & [(CH_3)_2N]Cl_2P = NP(S)[N(CH_3)_2]_2 \\ (XI) & (XI') \\ & [(CH_3)_2N]_3P = NP(S)Cl_2 \\ (XI'') \end{array}$$

The ³¹P NMR spectrum is an AB quadruplet with centers at 26.1 and 60.6 ppm (J_{PNP} = 42.7 Hz). These data permit us to exclude XI' and XII" and select XI, which is confirmed by PMR. The doublets with δ 2.87 and 2.79 ppm in 2:1 ratio must be assigned to the dimethylamine groups at the imidated and the thiophosphoryl P.

Compound I reacts with dimethylamine at 1:8 ratio at -10 to -15° C to form a substance whose ³¹P NMR spectrum shows signals in the 23.7 and 63.7 ppm regions ($J_{PNP} = 41.5 \text{ Hz}$). In the PMR spectrum the presence of two doublets of approximately equal intensity permits us to assign the structure of tetramethylamido(tetramethylamidothiophosphorylimido)chlorophosphate, XII.

 $[(CH_3)_2N]_2ClP = NP(S)[N(CH_3)_2]_2$ (XII)

The replacement of Cl in XII by a dimethylamino group goes slowly, 24-48 h at ~20°C. The structure of imidophosphate III, which is formed in good yield, is confirmed by IR, PMR, and NMR spectra and elemental analysis. Compound III was also obtained from hexamethyltriamidophosphate and tetramethyldiamidoazidophosphate [7]:

The physical constants and the spectral characteristics of the materials obtained by the two methods (see Tables 1 and 2) coincide. Analogously, XII reacts with diethylamine or morpholine:

 $\begin{array}{l} (\text{XII}) + 2\text{R}_{2}\text{NH} \rightarrow [(\text{CH}_{3})_{2}\text{N}]_{2}(\text{R}_{2}\text{N})\text{P} = \text{NP}(\text{S})[\text{N}(\text{CH}_{3})_{2}]_{2} \quad (\text{XIII}), \text{ (XIV)} \\ \text{R} = \text{C}_{2}\text{H}_{5} \text{ (XIII)}; \begin{array}{c} \text{NCH}_{2}\text{CH}_{2}\text{OCH}_{2}\text{CH}_{2} \text{ (XIV)}. \end{array}$

Thus, the reaction of I with dimethylamine may be described by the following scheme:

 $(I) + 4 (CH_{3})_{2}NH - | \xrightarrow{} [(CH_{3})_{2}N]_{2}CIP = NP(S)CI_{2} \xrightarrow{} [(CH_{3})_{2}N]_{2}CIP = NP(S)CI[N(CH_{3})_{2}] \xrightarrow{} [(CH_{3})_{2}N]_{2}CIP = NP(S)CI[N(CH_{3})_{2}] \xrightarrow{} (CH_{3})_{2}NH \xrightarrow{} [(CH_{3})_{2}N]_{2}CIP = NP(S)CI[N(CH_{3})_{2}] \xrightarrow{} (CH_{3})_{2}NH \xrightarrow{} [(CH_{3})_{2}N]_{2}CIP = NP(S)[N(CH_{3})_{2}] \xrightarrow{} (CH_{3})_{2}NH \xrightarrow{} (III)$

The results are apparently to be explained by the reduced reactivity of the Cl atoms when dimethylamino groups have been introduced into the molecule. Thus, the presence of two dimethylamino groups at the imidated P atom sharply reduces the reactivity of the tertiary Cl, and subsequent replacement by dimethylamine occurs at the Cl atoms attached to the thiophosphoryl P.

Compound I reacts readily with diethylamine. At 1:2 reagent ratio, diethylamido(dichlorothiophosphorylimido)dichlorophosphate (XV) is formed. The same substance is obtained by the reaction of I and diethylaminotrimethylsilane in a 1:1 ratio:

(I) +
$$2(C_2H_5)_2NH \rightarrow [(C_2H_5)_2N]Cl_2P = NP(S)Cl_2 \leftarrow (CH_3)_3SiN(C_2H_5)_2 + (I)$$

(XV)

In the ³¹P NMR spectra of the substances obtained by the two methods, the signals in the 31.0 ppm region indicate the presence of a dichlorothiophosphoryl group. This conclusion was confirmed by the synthesis of XV from diethylamido(dichlorophosphorylimido)dichlorophosphate and P_2S_5 . The physical constants are given in Table 1; the spectral characteristics, in Table 2.

Compound I reacts with diethylamine, 1:4, to form the disubstituted product, according to elemental analysis; the ³¹P NMR spectrum lacks the dichlorothiophosphoryl signal in the 29-31 ppm region. The signals

in the 1.8 and 53.9 ppm regions permit us to assign the structure of diethylamido(diethylamidochlorothiophosphorylimido)dichlorophosphate (XVI):

$[(C_2H_5)_2N]Cl_2P = NP(S)Cl[N(C_2H_5)_2]$ (XVI)

In this reaction the preferred formation of XVI apparently is to be ascribed to the fact that diethylamine is more nucleophilic than dimethylamine.

EXPERIMENTAL

IR spectra were obtained on a UR-20 apparatus in a liquid film; for imidophosphates II and III, in a KBr tablet. PMR spectra were obtained on a Perkin Elmer R-12 apparatus in CCl_4 relative to TMS. ³¹P NMR spectra were obtained on a Brucker HX-90 apparatus (36, 43 Hz) with quenching of the P-proton interaction; the internal standard was 85% H₃PO₄.

<u>Reaction of Thiopentachloride I with Alcohols</u> (general method). To a solution of 0.05-0.08 mole of I in 25-75 ml of CH_2Cl_2 at ~20°C was added, with mixing, an equimolar amount of methanol (ethanol, or butanol) in 5-10 ml of CH_2Cl_2 . After several hours the solvent and the volatile materials were evaporated in vacuum, and the residue was distilled. When the reaction was carried out in methanol, the NMR spectrum of the reaction mixture before distillation showed signals with $\delta - 0.4$ (P') and 28.2 ppm (P") (J_{PNP} = 7.3 Hz), that belong to IVa; with butanol, $\delta - 0.4$ and 30.0 ppm (J_{PNP} = 22 Hz), corresponding to IVc.

From 19.2 g of I and 2.22 g of methanol there was obtained 11.6 g (61%) of Va, bp 132-135°C (0.5 mm), nD²⁰ 1.5666, d₄²⁰ 1.7346. Found: P 21.6; S 12.1%. CH₃Cl₄NOP₂S. Calculated: P 22.0; S 11.4%. IR (ν , cm⁻¹): 1320 (P= N), 1250 (P=O), 460 (PCl). ³¹P NMR (δ , ppm): 30.1 (P'), -11.7 (P") (J_{PNP} = 4.9 Hz).

From 13.8 g of I and 2.22 g of ethanol there was obtained 8.6 g (60%) of Vb, bp 105°C (0.005 mm), n_D²⁰ 1.5604, d₄²⁰ 1.6285. Found: Cl 48.0; S 10.9%. C₂H₅Cl₄NOP₂S. Calculated: Cl 48.1; S 11.4%. IR (ν, cm⁻¹): 1315 (P=N), 1260 (P=O), 470 (PCl). ³¹P NMR (δ, ppm): 27.3 (P'), -12.5 (P") (J_{PNP} = 7.6 Hz).

Analogously from 23.6 g of I and 6.1 g of butanol there was obtained 17.1 g (68%) of Vc, bp 105°C (0.005 mm), n_D^{20} 1.5452, d_4^{20} 1.5022. Found: P 10.4%. $C_4H_9Cl_4NOP_2S$. Calculated: P 9.9%. IR (ν , cm⁻¹): 1325 (P=N), 1260 (P=O), 470 (PCl). ³¹P NMR (δ , ppm): 27.3 (P'), -12.5 (P") (J_{PNP} = 7.3 Hz).

Phenyl (Dichlorothiophosphorylimido)dichlorophosphate (VI). A) Compounds I (8.7 g) and 2.9 g of phenol were heated at 140-150°C until gas evolution ceased. After distillation there was obtained 7.0 g of VI.

B) A mixture of 21.7 g of phenyl (dichlorophosphorylimido)dichlorophosphate and 3.2 g of P_2S_5 was heated at 150-160°C to complete dissolution (4-5 h). The pressure was gradually reduced and the volatile products were distilled, bp < 120°C (0.5 mm). The fraction distilling at >120°C (0.5 mm) was redistilled. Compound VI (6.8 g) was obtained.

<u>Diphenyl (Dichlorothiophosphorylimido)chlorophosphate (VII)</u>. Compound I (11.3 g) and 7.5 g of phenol were heated and held at 160-170 °C for 4-5 h until HCl evolution ceased. After distillation 11.7 g of VII was obtained.

<u>Triphenyl (Dichlorothiophosphorylimido)phosphate (VIII)</u>. To a mixture of 10.5 g of phenol and 10.5 g of I were added several drops of pyridine. The mixture was heated slowly for 1 h, and held for 2 h at 180-185°C, then for 1 h at 200-205°C. After distillation, 10.6 g of VIII was obtained.

Triphenyl (Diphenoxythiophosphorylimido)phosphate (II). A) To a mixture of 9.5 g of I and 15.8 g of phenol were added several drops of pyridine. The mixture was held for 3 h at 180°C, 2 h at 200°C, and 1 h at 230-240°C until HCl evolution nearly ceased. The mixture was cooled and treated with 10 ml of methanol, and the crystalline precipitate was filtered off and washed with cold methanol. Compound II (4.9 g) was obtained.

B) Triphenyl phosphite (7.0 g) and 5.9 g of diphenyl azodithiophosphate, and 2.0 ml of benzene were mixed and heated slowly with stirring to 95°C. After the reaction was over, the volatile materials were driven off, and the residue was recyrstallized from 1:1 acetone:hexane. There was obtained 10.2 g (89%) of II, mp 96-98°C. Found: P 10.8; S 6.1%. $C_{30}H_{25}NO_5P_2S$. Calculated: P 10.8; S 5.6%.

 $\frac{\text{Dimethylamido(dichlorothiophosphorylimido)dichlorophosphate (IX). A) To a solution of 21.6 g of I in 100 ml of abs. ether was added 6.8 g of dimethylamine in 100 ml of ether at -10 to -5°C with stirring. The filtrate was evaporated. After distillation 16.4 g of IX was obtained.$

B) A mixture of 14.5 g of dimethylamido(dichlorophosphorylimido)phosphate and 2.6 g of P_2S_5 was heated at 150-160°C for 2-3 h to complete dissolution. The pressure was lowered gradually and the fraction boiling at > 95°C (0.2 mm) was distilled. After redistillation 3.4 g of IX was obtained.

 $\frac{\text{Tetramethyldiamido}(\text{dimethylamidochlorothiophosphorylimido})\text{chlorophosphate}(XI). \text{ To a solution of } 28.6 \text{ g of I in 150 ml of abs. ether was added 27.0 g of dimethylamine in 100 ml of ether at -15 to -10 °C with stirring. The mixture was stirred for 1 h at -10 to 0 °C, and 1 h at 0 to 10 °C, and the filtrate was evaporated. After distillation 20.5 g of X was obtained.}$

 $\frac{\text{Tetramethyldiamido}(\text{tetramethyldiamidothiophosphorylimido})\text{chlorophosphate (XII). To 25.4 g of I}{\text{in 200 ml of abs. ether was added 35.0 g of dimethylamine in 100 ml of ether at -10 to -5°C. The mixture was held for 1 h at that temperature, the hydrochloride was separated, and the filtrate was evaporated. After two distillations 14.0 g of XII was obtained.}$

Reaction of XII with Amines. A mixture of 7.8 g of XII in 25 ml of abs. ether and 3.6 g of dimethylamine was held at $\sim 20^{\circ}$ C in a sealed ampul for 48 h. The precipitate was separated and the residue was distilled. There was obtained 6.1 g of hexamethyltriamido(tetramethyldiamidothiophosphorylimido)phosphate (III).

Analogously, from 6.0 g of XII and 6.0 g of diethylamine there was obtained 5.4 g of tetramethyldiamidodiethylamido(tetramethyldiamidothiophosphorylimido)phosphate (XIV).

<u>Diethylamido(dichlorothiophosphorylimido)dichlorophosphate (XV)</u>. A) To 8.2 g of I in 100 ml of abs. ether at -10 to 15° C was added 4.2 g of diethylamine in 10 ml of ether. The precipitate was removed and the filtrate was evaporated. After distillation 6.4 g of XV was obtained.

B) To a solution of 13.3 g of I in 50 ml of abs. CH_2Cl_2 at -10°C was added 6.9 g of diethylaminotrimethylsilane. The mixture was stirred for 1 h at -10°C and for 2 h at ~20°C. After the volatile materials were driven off the residue was distilled. There was obtained 11.0 g of XV.

C) A mixture of 22.1 g of diethylamido(dichlorothiophosphorylimido)dichlorophosphate and 3.9 g of P_2S_5 was heated to 150-160°C. After the P_2S_5 dissolved, the pressure was gradually reduced, the volatile materials were driven off, and the residue was distilled. There was obtained 9.6 g of XV.

<u>Diethylamido(diethylamidochlorothiophosphorylimido)dichlorophosphate (XVI)</u>. To 20.8 g of I in 100 ml of ether at -10 to -5° C was added 21.4 g of diethylamine. The mixture was stirred for 2 h at $\sim 20^{\circ}$ C and left to stand over night, the precipitate was separated, and the filtrate was evaporated. After two distillations 10.1 g of XVI was obtained.

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CONCLUSIONS

1. In the reaction of the thiopentachloride with nucleophilic reagents (alcohols, phenol, dialkylamines, diethylaminotrimethylsilane), there occurs first of all the replacement of the first chlorine atom at the imidated phosphorus. Subsequent replacement of chlorine depends on the nature of the entering group; with phenol, it occurs at the imidated phosphorus, whereas with dialkylamines it can occur either at the imidated phosphorus or the thiophosphoryl phosphorus.

2. Replacement of oxygen by sulfur can occur in the reaction of phosphorylimidophosphates, $R_3P = N - P(O)R_2$, with phosphorus pentasulfide.

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