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REACTION OF DICHLOROPHOSPHORYLIMIDOPHOSPHORUS TRICHLORIDE  
WITH NUCLEOPHILIC REAGENTS

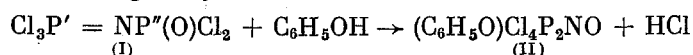
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Dichlorophosphorylimidophosphorus trichloride ("pentachloride"),  $\text{Cl}_3\text{P}=\text{NP}(\text{O})\text{Cl}_2$  (I), is an intermediate for the synthesis of insecticides, oil additives, plasticizers, and corrosion inhibitors [1]. A systematic study of its chemical properties has not been made up to now. The products of replacing all of the chloride atoms by anilide [2], p-nitrophenoxy [2], dimethylamido [3], and alkoxy [4] groups have been described. The monoalkoxy derivatives of the pentachloride were described in [6].

The reaction of pentachloride (I) with phenols, amines, and their derivatives, was studied in the present paper in order to expand the methods for the synthesis of phosphorylimidophosphorus compounds of general formula  $\text{R}_3\text{P}=\text{NP}(\text{O})\text{R}_2$ , and also to determine the order of replacing the Cl atoms.

When (I) is heated with phenol, using a 1:1 ratio of the reactants, the monophenoxy derivative (II) is obtained in good yield:



It is possible to propose two structures for (II):  $(\text{C}_6\text{H}_5\text{O})\text{Cl}_2\text{P}=\text{N}-\text{P}(\text{O})\text{Cl}_2$  (IIA) and  $\text{Cl}_3\text{P}=\text{NP}(\text{O})\text{Cl}(\text{OC}_6\text{H}_5)$  (IIB).

The IR spectral data (presence of absorption in the vicinity of 1350 and 1275  $\text{cm}^{-1}$ , which is characteristic for the  $\text{P}=\text{N}$  and  $\text{P}=\text{O}$  groups of the conjugated  $\text{P}=\text{N}-\text{P}=\text{O}$  fragment) do not permit choosing between structures (IIA) and (IIB). The  $^{31}\text{P}$  NMR spectrum of (II) consists of two doublets at -2.3 and -13.1 ppm ( $J_{\text{PNP}} = 51.3$  Hz) and is in agreement with formula (IIA). The signals of the P atoms of the starting pentachloride are found in the vicinity of  $\delta\text{P}' 0.9$  and  $\delta\text{P}'' - 12.5$  ppm [7]. The decision in favor of structure (IIA) is also confirmed by the data of the  $^{35}\text{Cl}$  NQR spectrum, which consists of three lines with the frequencies  $\nu_1 26.758$ ,  $\nu_2 27.192$ , and  $\nu_3 28.527$  MHz, with the relative intensities equal to 1:1:2. The signals in the vicinity of 26.758 and 27.192 MHz are characteristic for Cl atoms on the phosphoryl P atom, while the signal at 28.527 MHz is characteristic for a Cl on an imido P atom. The average frequencies of the Cl atoms of (dichlorophosphorylimido)methyl dichlorophosphonate,  $\text{CH}_3\text{Cl}_2\text{P}=\text{N}-\text{P}(\text{O})\text{Cl}_2$ , are found in the vicinity of  $\nu_{\text{av}} 28.075$  MHz for the Cl at  $\text{P}=\text{N}$ , and  $\nu_{\text{av}} 26.343$  MHz for the Cl at  $\text{P}=\text{O}$  [8].

Compound (I) reacts in a similar manner with halo-substituted phenols, but the yield of the corresponding monosubstituted derivatives is substantially lower:



Here X = o-, m-, p-Cl, o-, m-, p-Br, p-F. The yields, constants, and the IR and  $^{31}\text{P}$  NMR spectral data for the obtained compounds are given in Table 1.

Compound (I) does not react with p-nitrophenol at 160°C, while the reaction mixture decomposes at a higher temperature.

The second Cl atom of pentachloride (I) can be replaced by the phenoxy group at 150-160°, and here O,O-diphenyl(N-dichlorophosphorylimido)chlorophosphate (III) is obtained in good yield, whose structure was proved via the IR and  $^{31}\text{P}$  NMR spectral data (Table 2).

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TABLE 1. Monoaroxy Derivatives of Dichlorophosphorylimidophosphorus Trichloride

Com- pound	Ar	Yield, %	bp, °C (p, mm Hg)	<sup>30</sup> <i>n</i> <sub>D</sub>	<i>d</i> <sub>4</sub> <sup>20</sup>	Found		Empirical formula	Infrared spectrum, <i>ν</i> , cm <sup>-1</sup>		<sup>31</sup> P NMR spectrum		
						Calculated	%		P=N	P=O	δ, ppm	<i>J</i> , Hz	P'
(II)	C <sub>6</sub> H <sub>5</sub>	84 *	103-105(0,004)	1,5519	-	42,1 41,8	18,3 18,3	C <sub>6</sub> H <sub>5</sub> Cl <sub>4</sub> NO <sub>2</sub> P <sub>2</sub>	1350	1275	-2,3	-13,1	54,3
(IIa)	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub>	45	123-125(0,004)	1,5611	-	17,1 17,1	17,1 17,1	C <sub>6</sub> H <sub>4</sub> Cl <sub>5</sub> NO <sub>2</sub> P <sub>2</sub>	1350	1270	-3,1	-12,6	33,3
(IIb)	<i>m</i> -ClC <sub>6</sub> H <sub>4</sub>	31	115-116(0,005)	1,5620	1,6517	48,8 49,1	17,1	C <sub>6</sub> H <sub>4</sub> Cl <sub>3</sub> NO <sub>2</sub> P <sub>2</sub>	1340	1270	-1,9	-12,7	36,0
(IIc)	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	35	121-123(0,003)	1,5617	1,6507	17,1 17,1	17,1 17,1	C <sub>6</sub> H <sub>4</sub> Cl <sub>3</sub> NO <sub>2</sub> P <sub>2</sub>	1345	1270	-2,7	-12,2	34,5
(II d)	<i>o</i> -BrC <sub>6</sub> H <sub>4</sub>	32	119-121(0,003)	1,5719	1,8242	15,4 15,4	15,4 15,4	C <sub>6</sub> H <sub>4</sub> BrCl <sub>3</sub> NO <sub>2</sub> P <sub>2</sub>	1345	1265	-2,0	-12,7	36,2
(II e)	<i>m</i> -BrC <sub>6</sub> H <sub>4</sub>	34	117-119(0,003)	1,5760	1,8206	15,0 15,4	15,0 15,4	C <sub>6</sub> H <sub>4</sub> BrCl <sub>3</sub> NO <sub>2</sub> P <sub>2</sub>	1345	1270	-2,1	-12,7	36,1
(II f)	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	38 *	119-121(0,004)	-	-	15,9 15,9	15,9 15,9	C <sub>6</sub> H <sub>4</sub> BrCl <sub>3</sub> NO <sub>2</sub> P <sub>2</sub>	1350	1270	-	-	-
(II g)	<i>p</i> -FC <sub>6</sub> H <sub>4</sub>	49	110-112(0,009)	1,5390	1,6423	41,0 41,1	18,0 18,0	C <sub>6</sub> H <sub>4</sub> Cl <sub>4</sub> FNO <sub>2</sub> P <sub>2</sub>	1355	1270	-2,4	-12,0	33,6

\*Low-melting compounds that crystallize with difficulty.

TABLE 2. Di- and Triphenoxy Derivatives of Pentachloride (I) and Their Dimethylamides

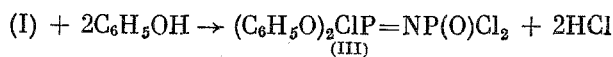
Com- pound	Formula	Yield, %	bp, °C (p, mm Hg)	$n_D^{20}$	$d_4^{20}$	Found Calculated, %			Infrared spectrum, $\nu$ cm <sup>-1</sup>			PMR spectrum, $\delta$ ppm <sup>31</sup> P NMR spectrum				
						P	N	Cl	P=N	P=O	(CH <sub>3</sub> ) <sub>2</sub> N N	(O) N	(C <sub>6</sub> H <sub>5</sub> )	P'	P''	JPNP, Hz
(III)	(C <sub>6</sub> H <sub>5</sub> O) <sub>2</sub> ClP'=NP''(O)Cl <sub>2</sub>	84	122-125 (0,001)	1,5632	1,4466	16,4 16,1		27,9 27,7	1360	1270	-	-	7,2- 7,4 m	-11,8	-12,8	45,5
(IV)	(C <sub>6</sub> H <sub>5</sub> O) <sub>2</sub> P'=NP''[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	59*	142-144 (0,001)	1,5398	1,4788	14,9 15,1	13,7 13,7		1330	1200	2,93 d	2,41 d	7,3 m	-7,2	9,3	51,3
	(CH <sub>3</sub> ) <sub>2</sub> N    O	69 †	142-144 (0,001)	1,5404	1,4816		13,9 13,7		1330	1200	2,95 d	2,44 d	7,3 m	-7,1	9,4	51,5
(V)	(C <sub>6</sub> H <sub>5</sub> O) <sub>3</sub> P'=NP''(O)Cl <sub>2</sub>	76 ‡	165-170 (0,005)	1,5728	-	-	-	16,2 16,0	1350	1260	-	-	7,2- 7,4 m	-24,7	-12,3	51,3
(VI)	(C <sub>6</sub> H <sub>5</sub> O) <sub>3</sub> P'=NP''[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	40**	168-170 (0,004)	1,5567	1,2173	13,2 13,5	8,9 9,2		-	-	-	2,32 d	7,4 m	-24,1	9,8	48,8
		67 †	170-171 (0,003)	1,5575	1,2161	13,5 13,5	9,2 9,2		-	-	-	2,33 d	7,4 m	-24,1	9,8	48,8

\*Obtained by reacting imidophosphate (III) with dimethylamine.

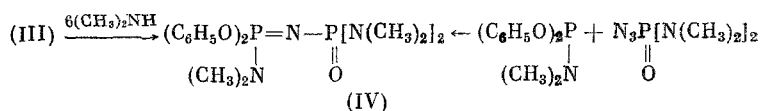
†Obtained by reacting (tetramethyldiamido)azidophosphate with the appropriate phosphines.

‡<sup>35</sup>Cl NQR spectrum:  $\nu_1$  27.076 MHz [9],  $\nu_2$  27.110 MHz [9], viscous liquid that crystallizes with difficulty.

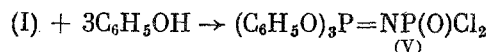
\*\*Reaction product of imidophosphate (VI) with dimethylamine.



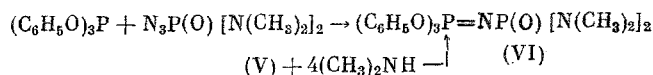
The presence of two phenoxy groups on the imido P atom can also be confirmed by comparing the constants and the IR and PMR spectra of the product, obtained by replacing the Cl atoms in (III) by dimethylamido groups, with the constants and the IR and PMR spectra of O,O-diphenyl N-dimethylamido(tetramethyldiamidophosphorylimido)phosphate (IV), which was obtained by counter synthesis (see Table 2).



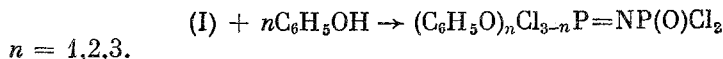
The reaction of (I) with phenol, using a 1:3 ratio of the reactants, at 180-200° gives triphenyl(dichlorophosphorylimido)phosphate (V):



To prove the structure of (V) we compared the IR and PMR spectra of triphenyl(tetramethyldiamidophosphorylimido)phosphate (VI), which was obtained from triphenyl phosphite and (tetramethyldiamido)azidophosphate, with those of the compound obtained from dichloride (V) and dimethylamine.



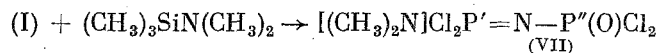
It proved that the IR and PMR spectra of the compounds, obtained by different methods, coincide, and their constants are also close (see Table 2). As a result, the reaction of (I) with phenol can be described by the following equation:



The found order of replacing the Cl atoms of pentachloride (I) by the phenoxy group can be explained by the fact that the latter does not substantially change the distribution of the electron density on the P atoms when compared with the starting (I). Consequently, it is the imido P atom of pentachloride (I) or its phenoxy derivatives that undergoes nucleophilic attack.

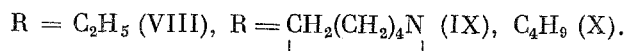
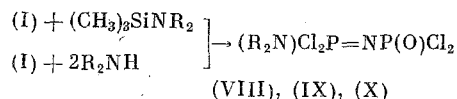
The fourth Cl atom in (I) is replaced under very drastic conditions (210-220°) to give, based on the <sup>31</sup>P NMR spectral data, a mixture of various compounds.

The reaction of (I) with dimethylaminotrimethylsilane proceeds very easily. Dimethylamido(N-dichlorophosphorylimido)dichlorophosphate (VII) is formed in good yield when the reactant ratio is 1:1.



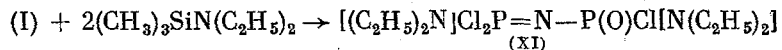
The structure of the obtained compound was confirmed by the IR, <sup>31</sup>P NMR, and <sup>35</sup>Cl NQR spectral data. Thus, the IR spectrum of (VII) has absorption bands in the vicinity of 1345 and 1260 cm<sup>-1</sup>, which are respectively characteristic for the P=N and P=O groups. The <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum of (VII) represents an AB quadruplet with δP' +7.8 and δP'' -11.5 ppm (J<sub>PNP</sub> = 29.3 Hz). The <sup>35</sup>Cl NQR spectrum consists of four lines (ν<sub>1</sub> 26.111, ν<sub>2</sub> 26.627, ν<sub>3</sub> 27.676, ν<sub>4</sub> 28.380 MHz) of equal intensity. The ν<sub>1</sub> and ν<sub>2</sub> frequencies should be assigned to the Cl atoms on the phosphoryl P atom, and the ν<sub>3</sub> and ν<sub>4</sub> frequencies to the Cl atoms on the imido P atom.

Compound (I) reacts in a similar manner with diethylaminotrimethylsilane, piperidinotrimethylsilane, and dibutylamine:



Product (VIII) was isolated when the pentachloride-diethylamine ratio was 1:2.

Pentachloride (I) reacts with diethylaminotrimethylsilane at a reactant ratio of 1:2 to give the disubstituted product. The presence of two doublets in the  $^{31}\text{P}$  NMR spectrum of the obtained compound in the vicinity of 4.0 and 1.7 ppm, with  $J_{\text{PNP}} = 35.4$  Hz testifies that the Cl atom of the dichlorophosphoryl group is also replaced by the dimethylamido groups:



Compound (XI) can be obtained in good yield by reacting (I) with diethylamine using a 1:4 ratio. The reaction of (I) with dimethylaminotrimethylsilane at a 1:2 ratio proceeds to give a mixture of compounds of unestablished structure.

Compounds (VIII)-(XI) react with Na alcoholates, with replacement of the Cl atoms by alkoxy groups. Thus, starting with compounds (VIII), (IX), and (XI), the products of reaction with BuONa were respectively: O,O-dibutyl N-diethylamido(dibutoxyphosphorylimido)phosphate (XII), O,O-dibutyl piperidido(dibutoxyphosphorylimido)phosphate (XIV), and O,O-dibutyl N-diethylamido(butoxydiethylamidophosphorylimido)phosphate (XV). In a similar manner, the reaction of (X) with EtONa gives O,O-dibutyl N-diethylamido(diethoxyphosphorylimido)phosphate (XIII). The constants of the obtained compounds are given in Table 3.

When compared with phenoxy groups, the different order of inserting a second diethylamido group into the (I) molecule can be explained by the increase in the electron density on the imido P atom, attached to the diethylamido group, as a result of which the Cl atom of the phosphoryl P atom is more amenable to nucleophilic substitution.

#### EXPERIMENTAL

The IR spectra were taken on a UR-20 instrument as a liquid film. The PMR spectra were taken on a Perkin-Elmer R-20 instrument in  $\text{CCl}_4$  solution and using TMS as the internal standard. The  $^{31}\text{P}$  NMR spectra were taken on a Bruker HX-90 instrument (36.43 MHz), with suppression of the couplings of the P atoms with the protons. The external standard was 85%  $\text{H}_3\text{PO}_4$  solution, and the values of the chemical shifts of the downfield signals are read as being positive. The  $^{35}\text{Cl}$  NQR spectra were taken on an ISSh-1 pulse instrument at  $-196^\circ\text{C}$ .

#### Reaction of Pentachloride (I) with Phenol or Its Derivatives (General Method)

A mixture of 0.03-0.08 mole of phenol (or its derivatives) and 0.03-0.08 mole of (I) was heated in an oil bath at  $120-130^\circ$  in the case of phenol (or at  $130-140^\circ$  in the case of its derivatives). When the brisk evolution of HCl had ceased, the mixture was kept for 2 h at  $160^\circ$  to remove the volatiles, and then the residue was vacuum distilled.

O,O-Diphenyl (N-Dichlorophosphorylimido)chlorophosphate (III). A mixture of 17.8 g of (I) and 12.3 g of phenol was heated in an oil bath at  $150-160^\circ$  until the HCl evolution ceased. Then it was kept at  $180^\circ$  until the volatiles were removed, followed by vacuum distillation of the residue to give 21.2 g of (III).

#### O,O-Diphenyl N-Dimethylamido(tetramethyldiamidophosphorylimido)phosphate (IV)

A. From (III). A solution of 5.1 g of dimethylamine in 50 ml of anhydrous ether was added at  $0-5^\circ$  to a solution of 5.4 g of chlorophosphate (III) in 50 ml of anhydrous ether. The residue from distilling off the volatiles was vacuum distilled to give 3.4 g of imidophosphate (IV).

B. From (Tetramethyldiamido)azidophosphate and O,O-Diphenyl N-Dimethylamidophosphite. A mixture of 4.5 g of the diphenyl dimethylamidophosphite and 2.9 g of (tetramethyldiamido)azidophosphate was cautiously heated to  $100^\circ$  and after brisk reaction had ceased (cooling is required) it was kept at  $110^\circ$  for 1 h to remove the volatiles, followed by vacuum distillation of the residue to give 4.6 g of (IV).

#### Triphenyl (Dichlorophosphorylimido)phosphate (V)

A mixture of 20.0 g of (I) and 21.4 g of phenol was heated for 1 h in an oil bath at  $170-180^\circ$ , and after the HCl evolution had ceased it was kept at  $200^\circ$  for 1 h. The residue from removal of the volatiles was vacuum distilled to give 24.8 g of (V).

#### Triphenyl (Tetramethyldiamidophosphorylimido)phosphate (VI)

A. From (V) and Dimethylamine. With cooling and stirring, to a solution of 12.0 g of (V)

TABLE 3. Amido Derivatives of Pentachloride (I) and Their Alkoxy Derivatives

Com- pound	Formula	Yield, %	bp, °C (p, mm Hg)	$n_D^{20}$	$d_4^{20}$	Found		Infrared spec- trum $\nu$ , cm <sup>-1</sup>		<sup>31</sup> P NMR spectrum		
						Calculated	P	P=N	P=O	$\delta$ , ppm	$J_{PNP}$ , Hz	
						Cl	P			P'	P''	
(VII)	$[(CH_3)_2N]Cl_2P'=NP''(O)Cl_2$	74	145-148(0,2)	-	-	51,4 51,0	22,1 22,3	1345	1260	7,8	-11,5	29,3
(VIII)	$[(C_2H_5)_2N]Cl_2P'=NP''(O)Cl_2$	90	96-99(0,004)	1,5114	1,4725	46,5 46,4	20,2 20,2	1335	1255	4,0	-12,1	26,9
(IX)	$[ \langle \text{C}_6\text{H}_5 \rangle N ] Cl_2P'=NP''(O)Cl_2$	50*	100-101(0,003)	1,5118	1,4720	-	20,1 20,2	1335	1255	4,0	-12,0	26,8
(X)	$[(C_4H_9)_2N]Cl_2P'=NP''(O)Cl_2$	73	180-182(0,5)	1,5339	1,5120	-	19,1 19,5	1340	1260	3,1	-12,1	-
(XI)	$[(C_2H_5)_2N]Cl_2P'=NP''(O)Cl[N(C_2H_5)_2]$	72*	173-175(0,5)	1,4995	1,2995	38,5 39,1	16,8 17,1	1340	1255	-	-	-
(XII)	$[(C_2H_5)_2N](C_4H_9O)_2P=NP(O)(OC_4H_9)_2$	54*	145-146(0,15)	1,5023	1,2774	30,5 31,0	18,0 18,1	1330	1255	4,0	4,7	35,4
(XIII)	$[(C_4H_9)_2N](C_2H_5O)_2P=NP(O)(OC_2H_5)_2$	51†	122-125(0,004)	1,4484	1,0072	-	13,6 13,7	1320	1220	-	-	-
(XIV)	$[ \langle \text{C}_6\text{H}_5 \rangle N ] (C_4H_9O)_2P'=NP''(O)(OC_4H_9)_2$	46	101-104(0,008)	1,4436	1,0518	-	15,4 15,5	1305	1240	-	-	-
(XV)	$[(C_2H_5)_2N](C_4H_9O)_2P=NP(O)(OC_4H_9)_2$ $N(C_2H_5)_2$	71	139-140(0,008)	1,4686	1,0835	-	13,1 13,2	1335	1240	-6,9	2,3	-
		61	115-117(0,004)	1,4541	1,0038	-	13,7 13,6	1320	1220	-	-	-

\*Reaction products of the "pentachloride" with the appropriate dialkylamines.

†Literature data [9]:  $n_D^{20}$  1.4465;  $d_4^{20}$  1.0074.

in 50 ml of abs. ether was added a solution of 5.4 g of dimethylamine in 50 ml of abs. ether. The mixture was stirred for 3 h at  $\sim 20^\circ$ . The residue from filtration and distilling off the volatiles was vacuum distilled to give 4.9 g of (VI).

B. From Triphenyl Phosphite and (Tetramethyldiamido)azidophosphate. A mixture of 6.9 g of triphenyl phosphite and 45 g of (tetramethyldiamido)azidophosphate was cautiously heated to  $110-120^\circ$ . At the end of reaction the mixture was kept for 3 h at  $140^\circ$ . After thorough removal of the volatiles the residue was vacuum distilled to give 6.8 g of (VI).

Dimethylamido(N-dichlorophosphorylimido)dichlorophosphate (VII). To a solution of 36.2 g of (I) in 50 ml of abs.  $\text{CH}_2\text{Cl}_2$  at  $-10$  to  $-15^\circ$  was added a solution of 14.8 g of dimethylaminotrimethylsilane in 20 ml of  $\text{CH}_2\text{Cl}_2$ . The mixture was kept for 1 h at  $\sim 20^\circ$ . Vacuum distillation gave 27.6 g of (VII).

#### Diethylamido(N-dichlorophosphorylimido)dichlorophosphate (VIII)

A. From (I) and Diethylaminotrimethylsilane. With stirring, to a solution of 20.4 g of (I) in 10 ml of abs.  $\text{CH}_2\text{Cl}_2$  at  $-10$  and  $-15^\circ$  was added 11.3 g of diethylaminotrimethylsilane. The mixture was kept for 1 h at  $\sim 20^\circ$  and then distilled to give 27.6 g of (VIII).

B. From (I) and Diethylamine. With stirring, to a solution of 23.4 g of (I) in 150 ml of abs. ether at  $-10$  to  $-15^\circ$  was added 12.8 g of diethylamine. The  $\text{Et}_2\text{NH}\cdot\text{HCl}$  was filtered, the filtrate was evaporated, and the residue was distilled to give 13.3 g of (VIII).

#### Piperidido(N-dichlorophosphorylimido)dichlorophosphate (IX)

To 19.3 g of (I) in 75 ml of abs.  $\text{CH}_2\text{Cl}_2$  at  $-10$  to  $-15^\circ$  was added 11.9 g of piperidinotrimethylsilane. The residue from distilling off the volatiles was distilled to give 17.2 g of (IX).

Dibutylamido(N-dichlorophosphorylimido)dichlorophosphate (X). To a solution of 11.2 g of (I) in 15 ml of abs. ether at  $-20$  to  $-15^\circ$  was added a solution of 5.6 g of dibutylamine and 4.5 g of triethylamine in 10 ml of ether. After distillation we obtained 11.5 g of (X).

#### Diethylamido(N-diethylamidochlorophosphorylimido)dichlorophosphate (XI)

A. From (I) and Diethylaminotrimethylsilane. With cooling and stirring, to a solution of 24.9 g of (I) in 40 ml of  $\text{CH}_2\text{Cl}_2$  was added 27.9 g of diethylaminotrimethylsilane. The mixture was kept for 2 h at  $30-35^\circ$ , the solvent was distilled off, and the residue was distilled to give 22.7 g of (XI).

B. From (I) and Diethylamine. To a solution of 19.5 g of (I) in 100 ml of abs. ether was added at  $-10^\circ$  a solution of 21.1 g of diethylamine in 20 ml of ether. The mixture was kept for 3 h at  $\sim 20^\circ$ . The hydrochloride was filtered, the filtrate was evaporated, and the residue was vacuum distilled to give 13.5 g of (XI).

Reaction of Diethylamido(N-dichlorophosphorylimido)dichlorophosphate (VIII) with BuONa. With cooling and stirring, to a solution of 3.3 g of Na in 120-150 ml of abs. butanol was added 11.5 g of (VIII) in 10 ml of benzene. The mixture was kept overnight at  $\sim 20^\circ$ , centrifuged, the solvents were distilled off, and the residue was vacuum distilled to give 8.1 g of (XII).

In a similar manner, from 5.2 g of tetrachloride (IX) and BuONa we obtained 5.1 g of imidophosphate (XIII), from 23.2 g of tetrachloride (X) and EtONa we obtained 12.1 g of imidophosphate (XIII), and from 12.6 g of trichloride (XI) and BuONa we obtained 9.9 g of imidophosphate (XV).

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#### CONCLUSIONS

When dichlorophosphorylimidophosphorus trichloride is reacted with nucleophilic reagents (phenols, dialkylamines, and their trimethylsilyl derivatives), the first to be replaced is the chloride atom on the imido P atom. As the result of further reaction with phenol the substitution at the imido P atom continues, while when reaction is with diethylamine or diethylaminotrimethylsilane the chlorine atom on the phosphoryl P atom is replaced.

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## SYNTHESIS OF FORMYLCYCLOPENTADIENYLTRICARBONYLRHENIUM AND SOME OF ITS PROPERTIES

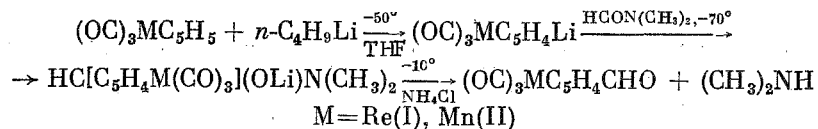
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Derivatives of  $\pi$ -cyclopentadienyltricarbonylrhenium (CTR) and -manganese (CTM), with a substituent in the  $\pi$ -cyclopentadienyl (CPD) ligand,\* have great importance for studying the comparative reactivity of a substituted CPD ligand. However, the low reactivity of the CPD ligand of CTR in electrophilic substitution reactions limits the possibility of obtaining the CPDP CTR, and consequently the synthesis of these compounds, based on the exchange reactions and subsequent transformations of the functional groups of the CPD ligands, assumes interest. The Li derivatives of CTR and formyl-CTR are especially interesting in this respect [1-6]. Detailed data are given in the present paper on the newly synthesized formyl-CTR.

The condensation of aliphatic and aromatic organolithium compounds with DMF proceeds in different solvents and in a broad temperature range to give the corresponding aldehydes [7].

The reaction of Li-CTR and Li-CTM with DMF was run in THF at  $-70^{\circ}\text{C}$  in order to ensure the stability of the Li compounds [3]. Under these conditions the Li derivatives of CTR and CTM react easily with DMF to give the aldehydes in respective yields of 91 and 75%.



This reaction made it possible to synthesize the previously unknown formyl-CTR and obtain the formyl-CTM in much higher yield than that reported in [8, 9].

$\text{LiAlH}_4$  in ether quantitatively reduces (I) at  $0^{\circ}$  to hydroxymethyl-CTR (III). The treatment of an alcohol solution of (I) with an  $\text{H}_2\text{SO}_4$  solution of 2,4-dinitrophenylhydrazine at  $20^{\circ}$  gave its 2,4-dinitrophenylhydrazone (IV). Similar to (II), compound (I) reacts with aniline at  $20^{\circ}$  to give the Schiff base (V) in 86% yield. The condensation of (I) with the acetyl derivatives of CTM, CTR, and ferrocene at  $20^{\circ}$ , in the presence of 20% NaOH solution, leads

\*The CTR derivatives, with a substituent in the CPD ligand, will be abbreviated as CPDP CTR.

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