

Studies of Organophosphorochloridates. Part V.† Some Derivatives of 2,4-Dichlorophenyl and Pentachlorophenyl Phosphorodichloridates

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The preparation and hydrolysis of 2,4-dichlorophenyl and pentachlorophenyl phosphorodichloridates are discussed. The phosphorodichloridates have been converted into some of the corresponding dialkyl phosphates, and *NN'*-dialkylphosphorodiamidates. The synthesis of 2,4-dichlorophenyl *N*-arylphosphoramidic chlorides and methyl 2,4-dichlorophenyl *N*-arylphosphoroamidates are also described. The pentachlorophenyl phosphorodichloridate derivatives were more fungicidal than those from 2,4-dichlorophenyl phosphorodichloridate.

2,4-DICHLOROPHENYL PHOSPHORODICHLORIDATE has been obtained by heating 2,4-dichlorophenol with phosphorus oxychloride either alone¹ or in the presence of magnesium chloride,² potassium chloride,³ or other group I metal chlorides.⁴ Our results support the observation⁴ that the effectiveness of these salts as catalysts increases with the atomic number of the metal.

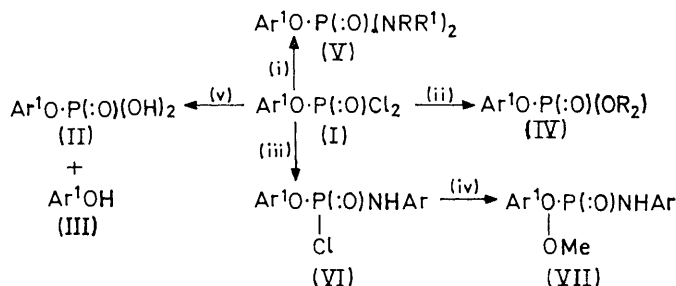
The preparation of pure pentachlorophenyl phosphorodichloridate has not been reported, though Bojars⁵ claimed that it is formed together with bispentachlorophenyl phosphorochloridate by heating pentachlorophenol with phosphorus oxychloride in presence of magnesium chloride. The phosphorochloridate is the sole product when the reaction is carried out using phosphorus oxychloride vapour on molten pentachlorophenol.⁶ We found that pure pentachlorophenyl phosphorodichloridate can be prepared by the action of phosphorus pentachloride on pentachlorophenol.

Pentachlorophenyl dihydrogen phosphate has been obtained⁷⁻⁹ by reaction of phosphorus pentachloride on tetrachlorobenzoquinone; and by dibenzyl phosphorochloridate on pentachlorophenol, followed by hydrolysis.¹⁰

Comparatively few derivatives of 2,4-dichlorophenyl phosphorodichloridate (I) have been reported. Hydrolysis to the dihydrogen phosphate (II) has been effected

by leaving the dichloridate (I) over aqueous sodium hydroxide *in vacuo*,¹¹ or by treatment with warm acid, alkali, or silver oxide-acetonitrile mixture.¹² All these methods also give some of the free phenol (III); however stirring with toluene containing 5% of water at 0° gave the phosphate as the sole product, though at higher temperatures the phenol was formed in substantial amounts.

Treatment of 2,4-dichlorophenyl phosphorodichloridate (I) with alcohols or phenols (2 molar equiv.) in



SCHEME

i, 5 RR'NH; ii, 2ROH-2C₆H₅N; iii, 2ArNH₂; iv, NaOMe-MeOH; v, H₂O. (Ar¹ = 2,4Cl₂C₆H₃⁻)

presence of pyridine gave the corresponding *OO'*-disubstituted phosphates ‡ [(IV) Table I].

⁵ N. Bojars, *Tech. Apskats.*, 1966, **52**, 7 (*Chem. Abs.*, 1968, **68**, 50,951k).

⁶ U.S.P. 2,710,269/1955 (*Chem. Abs.*, 1955, **49**, 12,851a).

⁷ T. Zincke and S. Kuster, *Ber.*, 1891, **24**, 927.

⁸ T. Zincke and O. Fuchs, *Annalen*, 1892, **267**, 1.

⁹ M. E. Barral, *Bull. Soc. Chim.*, 1895, **13**, 420.

¹⁰ A. J. Kirby and A. G. Varvoglis, *J. Amer. Chem. Soc.*, 1967, **89**, 415.

¹¹ D. M. Friedman and A. M. Seligman, *J. Amer. Chem. Soc.*, 1950, **72**, 624.

¹² K. Sasse, 'Methoden der Organischen Chemien,' Houben-Weyl, G. Theme-Verlag, Stuttgart, Germany, 1964, XII/2, 162.

† Part IV, R. J. W. Cremllyn, B. B. Dewhurst, and D. H. Wakeford, *J. Chem. Soc. (C)*, 1971, 3011.

‡ Attempted preparation of some higher dialkyl phosphates (IV) (R = cyclohexyl, benzyl, or lauryl) gave impure products since they could not be distilled without substantial decomposition.

¹ Fr.P. 1,009,362/1952 (*Chem. Abs.*, 1957, **51**, 18,632h).

² M. H. Maguire and G. Shaw, *J. Chem. Soc.*, 1953, 1479.

³ A. G. Varvoglis, *Chemika Chronika*, 1968, **33a**, 54 (*Chem. Abs.*, 1968, **69**, 106,075t).

⁴ V. V. Katyshkina and M. Y. Kraft, *Zhur. obshechi. Khim.*, 1956, **26**, 3060.

Treatment of the phosphorodichloridate (I) with the appropriate amine (5 molar equiv.) gave the corresponding *NN'*-dialkyl-2,4-dichlorophenyl phosphorodiamidate [(V) Table 2(a)]. Methyl 2,4-dichlorophenyl *N*-methylphosphoramidate has been prepared¹³ by successive treatment of the phosphorodichloridate (I) with methanol

has been obtained.¹⁶ In contrast, we synthesised the *OO'*-dimethyl and diethyl derivatives by heating pentachlorophenyl phosphorodichloridate with methanol or ethanol. Treatment with an excess of an aliphatic amine similarly afforded the corresponding pentachlorophenyl *NN'*-dialkylphosphorodiamidates [Table 2(b)].†

TABLE 1
Disubstituted 2,4-dichlorophenol phosphates, 2,4-Cl₂C₆H₃OP(:O)(OR)₂

R	B.p.	n _D ²⁰	ν _{P=O} (cm ⁻¹)	ν _{P-O-R} (cm ⁻¹)	Yield (%)	Mol. formula	Analysis							
							Found (%)				Required (%)			
							C	H	Cl	P	C	H	Cl	P
Me	150°/2.8 mm	1.5255	1255	1190	94	C ₈ H ₉ Cl ₂ O ₄ P	35.9	3.2	26.4	10.9	35.5	3.3	26.2	11.4
Et	169/4 mm	1.5050	1262	1170	90	C ₁₀ H ₁₃ Cl ₂ O ₄ P	40.4	4.5	23.8	10.5	40.1	4.3	23.7	10.3
Pr ^a	172—174/ 1.4 mm	1.5010	1262	1150	92	C ₁₂ H ₁₇ Cl ₂ O ₄ P	44.3	5.3	22.0	9.7	44.0	5.2	21.7	9.4
Bu ^a	196/3.5 mm	1.5022	1262	1150	91	C ₁₄ H ₂₁ Cl ₂ O ₄ P	47.7	6.1	20.2	8.3	47.3	5.9	20.0	8.7

TABLE 2(a)
2,4-Dichlorophenyl *NN'*-disubstituted phosphorodiamidates, 2,4-Cl₂C₆H₃·OP(:O)(NR¹R²)₂

R ¹	R ²	M.p. or B.p.	n _D ²⁰	ν _{P=O} (cm ⁻¹)	ν _{P-N} (cm ⁻¹)	Yield (%)	Mol. formula	Analysis									
								Found (%)					Required (%)				
								C	H	Cl	N	P	C	H	Cl	N	P
H	PhNH	150— 151°		1258	830	72	C ₁₃ H ₁₁ Cl ₂ N ₄ O ₂ P	51.4	4.2	16.8	13.5	7.6	51.1	4.0	16.8	13.2	7.3
H	Me	111— 111.5		1258	820	72	C ₈ H ₁₁ Cl ₂ N ₂ O ₂ P	36.0	4.2	26.3	10.5	12.0	35.7	4.1	26.4	10.4	11.5
H	Et	61—61.5		1255	830	75	C ₁₀ H ₁₃ Cl ₂ N ₂ O ₂ P	41.6	5.2	22.9	9.7	10.5	40.4	5.1	23.9	9.4	10.4
H	Pr ^a	209/ 0.8 mm	1.5270	1260	805	74	C ₁₂ H ₁₉ Cl ₂ N ₂ O ₂ P	43.9	5.6	25.2	7.8	7.6	44.3	5.8	21.8	8.6	9.5
H	Ph	165—167		1262	812	70	C ₁₈ H ₁₅ Cl ₂ N ₂ O ₂ P	54.9	4.1	18.1	7.1	6.5	55.0	3.8	18.1	7.1	7.9
H	PhCH ₂	97—97.5		1260	805	72	C ₂₀ H ₁₉ Cl ₂ N ₂ O ₂ P	59.8	4.6	17.1	6.8	7.4	57.0	4.5	16.9	6.7	7.3
Me	Me	164/ 0.5 mm	1.5277	1260	808	69	C ₁₀ H ₁₃ Cl ₂ N ₂ O ₂ P	40.8	5.4	23.9	9.3	11.2	40.4	5.05	23.9	9.4	10.4
H	C ₆ H ₁₁	136—138		1260	808	67	C ₁₈ H ₂₇ Cl ₂ N ₂ O ₂ P	53.5	6.9	17.3	6.9	7.5	53.3	6.7	17.5	6.9	7.65
Morpholino		212/ 0.9 mm	1.5272	1260	806	54	C ₁₄ H ₁₈ Cl ₂ N ₂ O ₄ P	43.8	5.4	18.4	6.9	7.55	44.1	5.0	18.6	7.35	8.1

TABLE 2(b)
Pentachlorophenyl *NN'*-dialkylphosphorodiamidates, C₆Cl₅·OP(:O)(NR¹R²)₂

R ¹	R ²	M.p.	ν _{P=O} (cm ⁻¹)	ν _{P-N} (cm ⁻¹)	Yield (%)	Mol. formula	Analysis									
							Found (%)					Required (%)				
							C	H	Cl	N	P	C	H	Cl	N	P
H	Me	188—189°	1360	835	60	C ₆ H ₅ Cl ₅ N ₂ O ₂ P	25.9	2.4	47.4	7.6	8.2	25.8	2.1	47.7	7.5	8.3
H*	Et	178—180	1360	830	62	C ₁₀ H ₁₂ Cl ₅ N ₂ O ₂ P	29.7	3.1	44.0	6.6	7.5	30.0	3.0	44.3	7.0	7.7
H	Pr ^a	153—154	1360	830	66	C ₁₂ H ₁₆ Cl ₅ N ₂ O ₂ P	33.4	3.6	41.4	6.7	7.0	33.6	3.7	41.4	6.5	7.2
Me	Me	144 (lit., ^{14,15} 144°)	1365	830	68	C ₁₀ H ₁₂ Cl ₅ N ₂ O ₂ P	29.8	3.0	44.2	7.0	7.5	30.0	3.0	44.3	7.0	7.7

* The most active compound against *S. aureus* and *C. globusum*

and methylamine. We obtained similar derivatives [(VII) Scheme] by reaction of the phosphorodichloridate (I) with an amine followed by treatment of the phosphoramidic chloride (VI) with sodium methoxide.

Some dialkyl pentachlorophenyl phosphates have been prepared^{14,15} by treatment of pentachlorophenol with the appropriate dialkyl phosphorochloridate; and with *NN'*-tetramethylphosphorodiamidic chloride, the corresponding pentachlorophenyl phosphorodiamidate

† A referee has suggested that these products might have the structure 4-R¹R²N-C₆Cl₄-O·P(:O)(Cl)NR¹R², formed by attack of the amine on the halogenated ring. However we consider that the phosphoryl chlorine atoms would be more reactive, and that our products accordingly have the structure depicted in Table 2(b)—they do not fume in moist air which suggests the absence of the P-Cl group.

The i.r. spectra of the 2,4-dichlorophenyl phosphorodichloridate derivatives showed the phosphoryl stretching band in the region 1270—1255 cm⁻¹, but in the derivatives of pentachlorophenyl phosphorodichloridate the phosphoryl stretching frequency increased to 1380—1360 cm⁻¹ in agreement with the observation^{17a} that the phosphoryl stretching frequency increases with

¹³ U.S.P. 2,971,974/1960 (*Chem. Abs.*, 1962, **56**, 14,171c).

¹⁴ D. Kh. Yarmukhametova and I. V. Cheplanova, *Izvest. Akad. Nauk. S.S.S.R., Ser. Khim.*, 1964, **11**, 1998 (*Chem. Abs.*, 1965, **62**, 7667g).

¹⁵ A. V. Starkov, I. A. Shenkman, M. P. Bogomolava, and P. Yu R¹ ilkov, *Zhur. obshchei. Khim.*, 1965, **35** (2), 352.

¹⁶ *Ima.* 920,117/1963 (*Chem. Abs.*, 1963, **59**, 5077d).

¹⁷ D. E. C. Corbridge, in 'Topics in Phosphorus Chemistry', eds. M. Grayson and E. J. Griffith, Interscience, New York, 1969, vol. 6 (a), p. 262; (b) p. 279; (c) p. 282; (d) p. 280.

increasing electronegativity of substituents. The *OO'*-dialkyl 2,4-dichlorophenyl- and pentachlorophenyl-phosphates showed the P-O-C (aliphatic) band in the range 1190—1150 cm^{-1} (see ref. 17b).

The derivatives of 2,4-dichlorophenyl- and pentachlorophenyl-phosphorodichloridates were examined by t.l.c. and, after purification, gave single spots. Pentachlorophenol and certain other chlorophenols are important industrial fungicides,¹⁸ it was, therefore, of interest to examine the phosphorylated derivatives for fungicidal activity. The compounds were screened as potential industrial fungicides.¹⁹ The pentachlorophenyl phosphorodichloridate derivatives were generally more active than the corresponding 2,4-dichloro-derivatives, which is in agreement with structure-activity studies of the fungitoxicity of various chlorinated phenols.¹⁸

Attempts to synthesise *P*¹*P*²-bis-(2,4-dichlorophenyl-*N*-phenylimido) pyrophosphate, by selective hydrolysis (aq. pyridine) of 2,4-dichlorophenyl-*N*-phenylimidophosphorochloridate, gave an impure product showing the P-O-P symmetrical stretching band at 940—930 cm^{-1} .^{17c}

Similar efforts to prepare the corresponding *N*-*p*-tolyl, and *N*-*p*-chlorophenyl pyrophosphates also failed to give pure products. *P*¹*P*²-bis-(2,4-dichlorophenyl) pyrophosphate has been isolated as the dicyclohexylammonium salt, by the action of dicyclohexylcarbodiimide on 2,4-dichlorophenyl dihydrogen phosphate.

EXPERIMENTAL

I.r. spectra were determined as Nujol mulls with a Unicam SP 200 spectrometer. M.p.s were obtained with a Kofler hot-stage apparatus. T.l.c. was carried out using silica gel G. plates developed with iodine vapour.

2,4-Dichlorophenyl Phosphorodichloridate.—Boiling phosphorus oxychloride (460 g) with 2,4-dichlorophenol (163 g) and potassium chloride (5 g) for 20 h gave the phosphorodichloridate (239 g, 86%), b.p. 136°/4.7 mm (lit.,²⁰ 70°/0.1 mm), n_D^{20} 1.5560 (lit.,²¹ 1.554) (Found: C, 25.4; H, 1.0; Cl, 50.6; P, 10.8. Calc. for $\text{C}_6\text{H}_3\text{Cl}_4\text{O}_2\text{P}$: C, 25.7; H, 1.1; Cl, 50.7; P, 11.0%), ν_{max} 1310 (P=O), 950 (P-O-C aromatic) cm^{-1} . The yield varied with different catalysts and reaction times: 65% with lithium chloride (6 h), 80% in 12 h; 70% with potassium chloride (6 h).

Bis-2,4-dichlorophenyl Hydrogen Phosphate.—The residue, after distillation of 2,4-dichlorophenyl phosphorodichloridate, was treated with sodium hydroxide as previously described² to give bis-2,4-dichlorophenyl hydrogen phosphate (6.5 g), m.p. 127—127.5° (lit.,² 131°) (Found: C, 37.2; H, 1.7; Cl, 36.5; P, 7.9. Calc. for $\text{C}_{12}\text{H}_7\text{Cl}_4\text{O}_4\text{P}_2$: C, 37.1; H, 1.8; Cl, 36.6; P, 7.9%).

Hydrolysis of 2,4-Dichlorophenyl Phosphorodichloridate.—The phosphorodichloridate (7.0 g) was stirred in toluene (20 ml) and water (1.0 ml) at 0° for 1 h. The precipitate was recrystallised from toluene to give 2,4-dichlorophenyl dihydrogen phosphate (5.8 g, 97%), m.p. 138—139° (lit.,¹¹ 138—139°) (Found: C, 29.2; H, 2.0; Cl, 29.3; P, 12.5).

* Formation of the copper-pyridine complex from a chloroform solution of the residue indicated the presence of free pentachlorophenol (0.02 g).

¹¹ Corden, in 'Fungicides,' ed. D. C. Torgeson, Academic Press, New York, 1969, vol. II, p. 484.

Calc. for $\text{C}_6\text{H}_5\text{Cl}_2\text{O}_4\text{P}$: C, 29.6; H, 2.1; Cl, 29.2; P, 12.7%). The hydrolysis was studied at different temperatures using the phosphorodichloridate (7 g) and water (20 ml) and no toluene. The yields of the phosphate were very low owing to its solubility in water. The optimum temperature was 0°, since the yields of isolated 2,4-dichlorophenol were 10.2% at 100°, 2.2% at 50°, and none at 0°.

Pentachlorophenyl Phosphorodichloridate.—An intimate mixture of powdered pentachlorophenol (13.3 g) and phosphorus pentachloride (15.8 g) were heated in an oil-bath at 190° for 1 h. Carbon tetrachloride was added to the cooled mixture and a stream of sulphur dioxide passed through the solution for 1 h. Evaporation under reduced pressure gave a residue (16 g), which after purification by repeated washing with light petroleum (b.p. 40—60°), gave the phosphorodichloridate (12 g), m.p. 98° (Found: C, 19.1; Cl, 64.4; P, 8.4. $\text{C}_6\text{Cl}_7\text{O}_2\text{P}$ requires C, 18.8; Cl, 64.8; P, 8.0%).

Pentachlorophenyl Dihydrogen Phosphate.—The phosphorodichloridate (3.4 g) was stirred with ether (10 ml) and water (1 ml) for 5 h at room temperature. Toluene (30 ml) was added, and the water was removed by azeotropic distillation. The residue* was dissolved in ether and reprecipitated with light petroleum (b.p. 60—80°) to give pentachlorophenyl dihydrogen phosphate (3.0 g, 95%), m.p. 208—210° (lit.,^{1,2} 203°) (Found: C, 20.8; H, 0.7; Cl, 51.0; P, 9.0. Calc. for $\text{C}_6\text{H}_2\text{Cl}_5\text{O}_4\text{P}$: C, 20.8; H, 0.6; Cl, 51.3; P, 8.9%), ν_{max} 1380 (P=O) and 1020 (P-OH) cm^{-1} .

Bis-pentachlorophenyl Hydrogen Phosphate.—Pentachlorophenol (26.6 g), phosphorus oxychloride (46 g), and potassium chloride (0.5 g) were boiled under reflux for 10 h with exclusion of moisture. The catalyst was removed, the filtrate evaporated under reduced pressure, and the residue crystallised from dioxan. Hydrolysis by treatment with water (50 ml) at 70—80° for 1 h gave bis-pentachlorophenyl hydrogen phosphate (30 g), m.p. 320—325° (Found: C, 24.5; H, 0.4; Cl, 59.3; P, 5.2. $\text{C}_{12}\text{HCl}_{10}\text{O}_4\text{P}_2$ requires C, 24.2; H, 0.2; Cl, 59.7; P, 5.2%).

Dialkyl 2,4-Dichlorophenyl Phosphates (Table 1).—A solution of 2,4-dichlorophenyl phosphorodichloridate (1 mol equiv.) in dry dioxan was added to a stirred solution of the alcohol (2 mol equiv.) and pyridine (2 mol equiv.). The mixture was stirred for 2 h at room temperature, and finally at 40° for 3 h. The solvent was evaporated under reduced pressure; the residue was extracted with ether, and the extract washed with water and evaporated. The residual liquid, by distillation under reduced pressure, gave the dialkyl 2,4-dichlorophenyl phosphate.

Dimethyl Pentachlorophenyl Phosphate.—A solution of pentachlorophenyl phosphorodichloridate (7.7 g) in ether (20 ml) was added to methanol (20 ml) with stirring. After 2 h at room temperature, the mixture was evaporated *in vacuo*. Recrystallisation of the residue from tetrahydrofuran-light petroleum (b.p. 60—80°) gave dimethyl pentachlorophenyl phosphate (5.6 g), m.p. 133—134° (lit.,¹⁴ 137—139°; lit.,¹⁵ 124—127°) (Found: C, 25.7; H, 1.6; Cl, 47.0; P, 7.8. Calc. for $\text{C}_8\text{H}_6\text{Cl}_5\text{O}_4\text{P}$: C, 25.6; H, 1.6; Cl, 47.4; P, 8.2%), ν_{max} 1380 (P=O) and 1180 (P-OMe) cm^{-1} . Reaction with ethanol, similarly gave the diethyl phosphate (64%), m.p. 112—113° (lit.,¹⁴ 115—116°; lit.,¹⁵ 110—112°).

¹⁹ D. M. M. Adema, G. M. Mejer, and H. J. Hueck, *Int. Biodeterioration Bull.*, 1967, **3** (1), 29.

²⁰ A. J. Kirby and W. P. Jencks, *J. Amer. Chem. Soc.*, 1965, **87**, 3209.

²¹ B.P. 644,467/1950 (*Chem. Abs.*, 1951, **45**, 3862g).

(Found: C, 30.2; H, 2.5; Cl, 44.2; P, 7.6. Calc. for $C_{10}H_{10}Cl_5O_4P$: C, 29.8; H, 2.5; Cl, 44.1; P, 7.7%).

2,4-Dichlorophenyl and Pentachlorophenyl NN'-Dialkylphosphorodiamidates [Tables 2(a) and 2(b)].—The phosphorodichloridate (1 mol equiv.) was added to a stirred solution of the appropriate amine (5 mol equiv.) in dioxan at 5° and the mixture was stirred at room temperature for 2 h, and finally at 40° for 2 h. The solvent was removed *in vacuo*, and the residue washed with water (to remove the amine hydrochloride). Recrystallisation from ethanol or aqueous ethanol gave the *NN'*-dialkylphosphorodiamidate.

Preparation of 2,4-Dichlorophenyl N-Arylphosphoramidic Chlorides (VI).—Aniline (4.7 g, 0.05 mol equiv.) was added to a stirred solution of 2,4-dichlorophenyl phosphorodichloridate (7.0 g, 0.025 mol equiv.) in dry benzene (150 ml) at 5°; the mixture was left overnight at room temperature. An excess hydrochloride was filtered off and, on cooling, the solution gave the *N-phenylphosphoramidic chloride* (7.0 g, 83%), m.p. 120–121° (Found: C, 42.7; H, 2.9; Cl, 32.0; N, 4.0; P, 9.3. $C_{12}H_9Cl_3NO_2P$ requires C, 42.8; H, 2.7; Cl, 31.7; N, 4.2; P, 9.2%), ν_{max} 1270 (P=O) and 822 (P-N) cm^{-1} . The following *N-arylphosphoramidic chlorides* were similarly prepared: *p-tolyl* (72%), m.p. 153–155° (Found: C, 44.6; H, 3.3; Cl, 30.2; N, 4.1; P, 8.6. $C_{13}H_{11}Cl_3NO_2P$ requires C, 44.5; H, 3.1; Cl, 30.4; N, 4.0; P, 8.8%), ν_{max} 1270 (P=O) and 830 (P-N) cm^{-1} ; *p-chlorophenyl* (73%), m.p. 157–159° (Found: C, 39.1; H, 2.5; Cl, 38.1; N, 3.8; P, 8.3. $C_{12}H_8Cl_4NO_2P$ requires C, 38.8; H, 2.2; Cl, 38.3; N, 3.8; P, 8.3%), ν_{max} 1270 (P=O) and 832 (P-N) cm^{-1} .

Methyl 2,4-Dichlorophenyl N-Phenylphosphoramidate (VII; Ar = Ph).—2,4-Dichlorophenyl *N-phenylphosphorochloridate* (3.4 g) was boiled under reflux with sodium methoxide (0.54 g) in methanol (20 ml) for 6 h. Methanol was distilled off and the residue was washed with water, dried, and recrystallised from tetrahydrofuran to give *methyl 2,4-dichlorophenyl N-phenylphosphoramidate* (2.5 g, 75%), m.p. 56–58° (Found: C, 46.8; H, 3.9; Cl, 21.1;

N, 4.2; P, 9.2. $C_{13}H_{12}Cl_2NO_3P$ requires C, 47.0; H, 3.6; Cl, 21.4; N, 4.2; P, 9.3%). The *N-methyl* derivative was obtained as described by Neeley *et al.*²¹ (40%), m.p. 49–50° (lit.,²¹ 49–50°) (Found: C, 36.0; H, 3.8; Cl, 26.1; N, 5.3; P, 11.8. Calc. for $C_8H_{10}Cl_2NO_3P$: C, 35.5; H, 3.7; Cl, 26.3; N, 5.2; P, 11.4%).

Similarly were prepared: the *N-p-tolylphosphoramidate* (VII; Ar = *p*-MeC₆H₄, 75%), m.p. 83.5–84.5° (Found: C, 48.6; H, 4.0; Cl, 20.4; N, 3.9; P, 8.7. $C_{14}H_{14}Cl_2NO_3P$ requires C, 48.55; H, 4.0; Cl, 20.5; N, 4.0; P, 9.0%), ν_{max} 1260 (P=O), 1222 (P-OMe), and 835 (P-N) cm^{-1} ; and the *N-p-chlorophenylphosphoramidate* (VII; Ar = *p*-ClC₆H₄, 68%), m.p. 107–108° (Found: C, 42.1; H, 3.0; Cl, 29.1; N, 3.7; P, 8.2. $C_{13}H_{11}Cl_3NO_3P$ requires C, 42.6; H, 3.0; Cl, 29.0; N, 3.8; P, 8.5%), ν_{max} 1260 (P=O), 1225 (P-OMe), and 825 cm^{-1} (P-N).

P³²-Bis-2,4-dichlorophenyl Dicyclohexylammonium Pyrophosphate.—2,4-Dichlorophenyl dihydrogen phosphate (2.4 g) in dry ether (20 ml) was treated with dicyclohexylcarbodi-imide (1.1 g) and the mixture was left 3 days at room temperature. The ether was removed under reduced pressure, and the viscous solid shaken with water (20 ml). Addition of cyclohexylamine to pH 8.5 gave a precipitate and recrystallisation from aqueous ethanol gave the *dicyclohexylammonium pyrophosphate* (1.8 g), m.p. 210–212° (Found: C, 43.0; H, 5.2; Cl, 20.9; N, 4.0; P, 9.0. $C_{24}H_{34}Cl_4N_2O_7P_2$ requires C, 43.3; H, 5.1; Cl, 21.3; N, 4.2; P, 9.3%), ν_{max} 940 cm^{-1} (P-O-P) (*cf.* i.r. of dicyclohexylammonium 2,4-dichlorophenyl phosphate in which this band was absent).

Thanks are due to Dr. J. M. C. Thompson of I.C.I. Ltd. (Nobel Division) for some of the microanalysis.

[1/1680 Received, 14th September, 1971]

²¹ W. B. Neeley, I. Ungar, E. H. Blair, and R. A. Nyquist *Biochemistry*, 1964, **3** (10), 1477.