

661. *Formation of Organo-phosphorus Compounds by the Reaction of Alkyl Chlorides with Phosphorus Trichloride in the Presence of Aluminium Chloride.**

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Many alkyl chlorides condense with phosphorus trichloride and aluminium chloride to form liquid or solid complexes, which when decomposed with water under controlled conditions give good yields of alkylphosphonyl dichlorides $R \cdot POCl_2$. *n*-Alkyl chlorides containing $\leq 3C$ give the corresponding *sec.*-alkylphosphonyl dichloride. By treatment with hydrogen sulphide the aluminium chloride complexes give successively alkylthiophosphonyl dichlorides $R \cdot PS_2Cl_2$ and dithiophosphoalkanes $R \cdot PS_2$. Evidence that the complexes are salt-like substances $[R \cdot PCl_3]^+[AlCl_4]^-$ is presented. Some reactions between alkyl chlorides and derivatives of phosphorus trichloride are also described.

CLAY (*J. Org. Chem.*, 1951, **16**, 892) prepared alkylphosphonyl dichlorides $R \cdot POCl_2$ by treating alkyl chlorides with phosphorus trichloride in the presence of aluminium chloride and decomposing the resulting complex with cold concentrated hydrochloric acid. This reaction has been observed independently by the present authors.

Ten alkyl chlorides, as well as cyclohexyl and benzyl chloride, reacted readily with phosphorus trichloride and aluminium chloride to give complexes which on treatment with water gave good yields of alkylphosphonyl dichlorides. *n*-Propyl, *n*-butyl, and *isobutyl* chloride yielded products identical with those obtained from *isopropyl*, *sec.*-butyl, and *tert.*-butyl chloride respectively with no trace of un-isomerised products. Although this isomerisation is somewhat analogous to that occurring when alkyl chlorides are condensed with benzene by the Friedel-Crafts reaction, the parallel is not complete, since, for instance, in the reaction between *n*-propyl chloride and benzene a mixture of *n*- and *isopropyl*benzene is always formed (Ipatieff, Pines, and Schmerling, *ibid.*, 1940, **5**, 253).

Vinyl chloride failed to react but allyl chloride gave a fair yield of allylphosphonyl dichloride ($CH_2:CH \cdot CH_2 \cdot POCl_2$) (contrast the isomerisation during Friedel-Crafts condensation).

Methylene chloride, chloroform, and carbon tetrachloride gave good yields of chloro-, dichloro-, and trichloro-methylphosphonyl dichloride respectively. Carbon tetrachloride was nearly as reactive as the alkyl monochlorides, but chloroform required refluxing for some hours to ensure complete reaction, and methylene chloride required heating at 100° in a closed vessel for 24 hours. Benzylidene dichloride and benzotrichloride also reacted similarly, provided that conditions were adjusted to minimise Friedel-Crafts condensation. On treatment with aniline the carbon tetrachloride derivative gave trianilinophosphine

* Cf., in part, B.P. Applns. 11,956/1948, 26,475/1951.

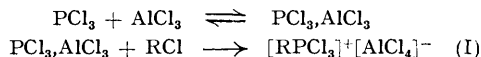
oxide, $(\text{NHP})_3\text{PO}$, instead of the dianilide afforded by most of the phosphonyl dichlorides, this being an example of the readiness (cf. Kamai, *Compt. rend. Acad. Sci. U.R.S.S.*, 1947, **55**, 219) with which the carbon-phosphorus bond, normally very stable, breaks when the carbon atom is attached to three chlorine atoms.

Ethylene dichloride and, especially, ethylidene dichloride, give good yields of phosphonyl dichlorides. *s*-Tetrachloroethane appeared to be quite unreactive and penta- and hexachloroethane, although appearing to form complexes, yielded no phosphonyl chloride. Instead in each case a quantity of phosphorus oxychloride was produced. Tri- and tetrachloroethylene appeared moderately reactive but, although the former yielded a small quantity of a phosphonyl chloride, the latter again produced only phosphorus oxychloride.

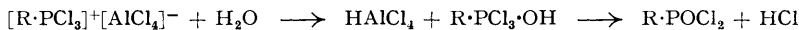
Attempts to make bisphosphonyl derivatives failed. Even 1 : 5-dichloropentane gave 4-chloro-1-methylbutylphosphonyl dichloride $\text{CH}_2\text{Cl}\cdot[\text{CH}_2]_2\cdot\text{CHMe}\cdot\text{POCl}_2$ with no trace of higher-boiling material.

A number of hydrocarbons substituted by bromine and fluorine were investigated. With the exception of chlorotrifluoromethane, which proved entirely unreactive, all gave products identical with those obtained from the corresponding chlorohydrocarbons, *e.g.*, chlorodifluoromethane gave dichloromethylphosphonyl dichloride.

Clay (*loc. cit.*) gives formula (I) for the complex formed in excellent yield by heating together equimolecular proportions of alkyl chloride, phosphorus trichloride, and aluminium chloride. This is borne out by the following observations: (1) Complexes, which although different in crystalline form were similar to the ethyl chloride complex in being crystalline solids of high melting point and in giving ethylphosphonyl dichloride on hydrolysis, were prepared either by adding aluminium chloride to ethylphosphorus tetrachloride $\text{Et}\cdot\text{PCl}_4$ or by passing chlorine into the complex of ethyldichlorophosphine $\text{Et}\cdot\text{PCl}_2$ and aluminium chloride. (2) The ethyl chloride complex was stable when heated for long periods with chlorohydrocarbons, *e.g.*, carbon tetrachloride. (3) Solutions of the complex in methylene chloride were readily electrolysed yielding, as the anode, aluminium chloride and, at the cathode, a product which although not precisely identified had the properties of an alkyl-dichlorophosphine $\text{R}\cdot\text{PCl}_2$. Support for this formula is also afforded by the existence of the analogous tetraphenylarsonium salt $[\text{Ph}_4\text{As}]^+[\text{AlCl}_5\text{Br}]^-$ which was shown by Lyon and Mann (*J.*, 1942, 666) to be formed by the action of bromobenzene on trichloro(triphenylarsine)aluminium ($\text{Ph}_3\text{As}\rightarrow\text{AlCl}_3$). The latter aluminium compound is a crystalline solid easily prepared by the addition of the two constituents. Although phosphorus trichloride and aluminium chloride do not give an analogous easily isolated compound, it is possible that a small degree of combination occurs, possibly in an equilibrium reaction. For the formation of (I) Clay suggested that the first stage was $\text{RCl} + \text{PCl}_3 \rightleftharpoons \text{R}\cdot\text{PCl}_4$. An alternative now proposed is:

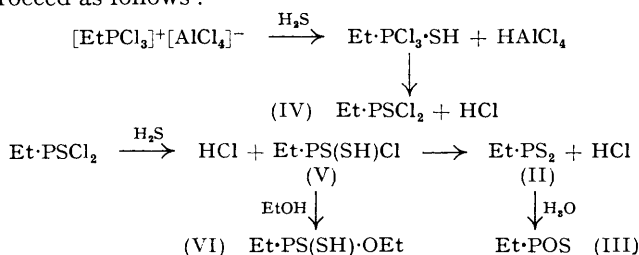


There is, however, insufficient evidence at present to decide between the two mechanisms. The hydrolysis mechanism suggested by Clay does not appear to be entirely satisfactory since it involves combination of a chlorine ion set free by the action of water on $[\text{AlCl}_4]^-$ with $[\text{R}\cdot\text{POCl}]^+$ produced by the action of water on $[\text{R}\cdot\text{PCl}_3]^+$. An alternative mechanism, as follows, appears more probable:



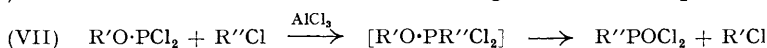
It appeared to be of interest to investigate the behaviour of the complexes with a reagent less vigorous than water. Hydrogen sulphide was found to react slowly with (I; $\text{R} = \text{Et}$) at about 130° with the evolution of hydrogen chloride. When the reaction was allowed to go to completion (several days), the main product after treatment with water was a colourless crystalline solid, $\text{C}_2\text{H}_5\text{PS}_2$, m. p. 157° , which in warm water gave a colourless solid, $\text{C}_2\text{H}_5\text{POS}$, m. p. $54-55^\circ$. It is doubtful whether the two compounds have these simple constitutions since the infra-red spectrum of the oxygen compound (personal communication from Mr. L. C. Thomas) does not contain the strong absorption band characteristic of the $\text{P}=\text{O}$ grouping (Meyrick and Thompson, *J.*, 1950, 229), and they have thus

probably cyclic structures. It is convenient, however, to refer to them as dithiophosphoethane (II) and thiophosphoethane (III) respectively. By stopping the reaction between (I) and hydrogen sulphide before completion, ethylthiophosphonyl dichloride (IV) was obtained. This sequence of reactions, by analogy with the hydrolysis mechanism already suggested, may proceed as follows:

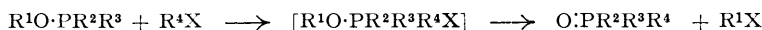


A derivative, *O*-ethyl hydrogen ethyldithiophosphonate (VI), of the postulated intermediate (V) was obtained by treating the mixed reaction products with ethyl alcohol.

A few experiments were performed to ascertain to what extent the ability to condense with alkyl chlorides was affected by substitution of the chlorine atoms in phosphorus trichloride by other atoms or groups. Dichlorophosphinous esters (VII) and alkyl chlorides in the presence of aluminium chloride readily gave alkylphosphonyl dichlorides $\text{R}\cdot\text{POCl}_2$. In this case the mechanism cannot have been that suggested for the phosphorus trichloride reactions, since this would have led to an ester of an alkylchlorophosphinic acid $\text{R}''\cdot\text{PO}(\text{OR}')\text{Cl}$; it must be assumed that the following reactions take place:



This mechanism conforms closely to that of an Arbusov rearrangement (von Kosopaloff, "Organophosphorus Compounds," J. Wiley & Son, New York, 1950, p. 121) which involves the reaction of an organic halide with a tervalent phosphorus ester to give a phosphine oxide:



This reaction has not hitherto been known to occur when R'' or $\text{R}''' = \text{halogen}$ and in the example just described it is evident that it is promoted by the aluminium chloride. When a *n*-alkyl halide takes part in a normal Arbusov rearrangement it does not undergo isomerisation and it is therefore of interest that *n*-propyl chloride produced *isopropyl*-phosphonyl dichloride. (Ethers also react with phosphorus trichloride and aluminium chloride to give alkylphosphonyl dichlorides, the ether presumably first reacting with phosphorus trichloride to give a dichlorophosphinous ester and an alkyl chloride, which then undergo the rearrangement just described.)

Ethyldichlorophosphine, in contrast to phosphorus trichloride, combines vigorously with aluminium chloride, and the product appears to react with ethyl chloride. No recognisable products, however, were isolated on hydrolysis. Although ethyl diethylphosphinate, $\text{Et}_2\text{PO}\cdot\text{OEt}$, was obtained by treatment of the reaction product with ethyl alcohol, it is probable that this arose by the formation of diethyl ethylphosphonite $\text{Et}\cdot\text{P}(\text{OEt})_2$, from unchanged ethyldichlorophosphine, which then underwent Arbusov rearrangement in the presence of ethyl chloride.

EXPERIMENTAL

The following procedures were used for the formation of aluminium chloride complexes (see Table). In each case the reaction was continued until all aluminium chloride had gone into solution.

A. The alkyl halide, phosphorus trichloride (or derivative), and aluminium chloride were mixed in that order and in the proportions indicated and shaken at room temperature, if necessary in a sealed vessel.

B. As A, except that the mixture was heated on the water-bath for a further period.

C. Aluminium chloride was suspended by continuous stirring in phosphorus trichloride,

No.°	Reagents		Mol. proportions RCl PXX'Cl	Mol. proportions AlCl ₃	Reaction conditions		Yield, calc. on PXX'Cl, %
	Alkyl halide	PXX'Cl X = X'			Complex formation	Hydrolysis, mols. H ₂ O	
1	MeCl	Cl	1-5	1-1	A (64 hrs.)	14	
2	EtCl	Cl	0-35	0-25	B (½ hr. ½ hr.)	2-8	
3	PrCl	Cl	0-30	0-50	A (1 hr.)	See note	
4	PrCl	Cl	0-25	0-50	B (1 hr. 1 hr.)	2-5	
5	CHMeEtCl	Cl	0-25	0-25	A (12 hrs.)	4-5	
6	BuCl	Cl	0-25	0-50	A (12 hrs.)	4-5	
7	BuCl	Cl	0-32	0-25	A (10 mins.)	3-5	
8	CHMe ₂ -CH ₂ Cl	Cl	0-25	0-5	A (1 hr.)	5-5	
9	CH ₃ -[CH ₂] ₁₅ -Cl	Cl	0-15	0-30	A (2 hrs.)	3-5	
10	C ₆ H ₁₁ Cl ^b	Cl	0-25	0-50	A (15 mins.)	5-0	
11	C ₆ H ₅ -CH ₂ -Cl	Cl	0-25	1-1	C (½ hr. 40°)	4-5	
12	CH ₃ -CHCl	Cl	—	1-1	F (1½ hrs. 40-50°)	5-0	
13	CH ₃ -CH-CH ₂ Cl	Cl	0-25	0-5	C (½ hr. 40-50°)	4-5	
14	CH ₂ Cl ₂	Cl	1-0	1-0	D (24 hrs.)	11	
15	CHCl ₃	Cl	0-5	0-25	E (10 hrs.)	3-0	
16	CCl ₄	Cl	0-35	0-25	E (1 hr.)	3-0	
17	(CH ₂ Cl) ₂	Cl	0-25	0-5	E (45 min.)	3-5	
18	CH ₃ -CHCl ₂	Cl	0-25	0-5	A (1 hr.)	3-5	
19	CHCl ₂ CCl ₂	Cl	0-25	0-25	D (12 hrs.)	2-0	
20	C ₆ H ₅ -CHCl ₂	Cl	0-25	1-0	C (½ hr. reflux)	3-5	
21	C ₆ H ₅ -CCl ₃	Cl	0-25	1-0	E (1½ hrs.)	4-5	
22	CH ₂ Cl-[CH ₂] ₃ -CH ₂ Cl	Cl	0-25	0-25	E (½ hr.)	3-0	
23	CHF ₂ Cl	Cl	—	0-25	F (60°)	4-5	
24	CF ₂ Cl ₂	Cl	0-5	0-5	F (60°)	4-5	
25	CH ₃ -F-CH ₂ Cl	Cl	0-21	0-5	E (1 hr.)	3-5	
26	CH ₃ -CFCl ₂	Cl	0-25	0-25	A (1½ hrs.)	4-5	
27	CH ₂ Br	Cl	0-25	0-5	E (3½ hrs.)	4-5	
28	CH ₂ ClBr	Cl	0-25	0-5	E (10 hrs.)	5-0	
29	CCl ₃ Br	Cl	0-25	0-25	E (2 hrs.)	4-5	
30	EtCl	F	0-5	0-25	A (6 days)	2-0	
31	EtCl	F	0-5	0-20	A (6 days)	2-0	
32	EtCl	Et	0-25	0-5	A (12 hrs.)	See note	
33	PrCl	Et	0-25	0-25	A (1 hr.)	3	
34	PrCl	OEt	0-25	0-25	D (5 hrs.)	See note	
35	PrCl	Et	0-30	0-25	D (1 hr.)	2-5	
36	BuCl	OPr	0-16	0-16	E (½ hr.)	2-0	

^a For notes see p. 3442.

Product

R in R-POCl ₂	B. p./mm.	Yield, calc. on PXX'Cl, %
Methyl	162°/760 m. p. 33°	68
Ethyl	34°/3	82
isoPropyl	35-5°/1-5	70
sec.-Butyl	35°/0-5	90
tert.-Butyl	59°/3	93
tert.-Butyl	57°/2	83
tert.-Butyl	m. p. 110°	81
tert.-Butyl	m. p. 110°	92
1-Methylpentadecyl	165°/1	60
cycloHexyl	90°/1	82
Benzyl	130°/2	62
1-Chloroethyl	m. p. 57-5°	Trace
Allyl	80-84°/15	53
Chloromethyl	55°/3	85
Dichloromethyl	50/0-5	63
Trichloromethyl	79/9	85
2-Chloroethyl	m. p. 156°	58
1-Chloroethyl	77°/6	75
2:2:2-Trichloroethyl	57°/3	20
2:2:2-Trichloroethyl	65-66°/1	20
α-Chlorobenzyl	132°/2	40
α-Chlorobenzyl	m. p. 48°	10
α-Chlorobenzyl	114-120°/2	15
4-Chloro-1-methylbutyl	112-123°/1	40
Dichloromethyl	67-70°/1	50
Trichloromethyl	m. p. 157-158°	35
2-Chloroethyl	63°/3	?
1:1-Dichloroethyl	m. p. 147-150°	35
Chloromethyl	66°/3	35
Chloromethyl	58°/2	35
Trichloromethyl	m. p. 152-162°	90
Ethyl	50-51°/6	22
"	88°/30	15
"	143°/1	13 g.
See note	—	—
See note	—	—
isoPropyl	62°/2	45
tert.-Butyl	m. p. 110°	75
cycloHexyl	—	—

Notes on Table.—(2) Found: Cl, 48.3. $C_2H_5OCl_2P$ requires Cl, 48.3%. The diethyl ester was obtained in 92% yield (calc. on phosphorus trichloride) directly from the complex by the method described below.

(3) The reaction product was stirred vigorously with carbon tetrachloride (800 ml.) and the suspension poured through several kg. of crushed ice.

(3) and (4) The dianilides when mixed had undepressed m. p. The dianilide of *n*-propylphosphonic acid prepared from *n*-propyl bromide *via* an Arbusov rearrangement has m. p. 150° (Ford-Moore, personal communication).

(5) and (6) The dianilides were identical (m. p. of mixture not depressed). The *n*-butylphosphonyl dianilide (Found: C, 66.1; H, 7.2. $C_{16}H_{21}ON_2P$ requires C, 66.8; H, 7.4%), prepared by treating with aniline the product obtained by refluxing diethyl *n*-butylphosphonate [prepared by Ford-Moore (unpublished result) from *n*-butyl bromide *via* an Arbusov rearrangement] with thionyl chloride, had m. p. 147—148° and depressed the m. p. of the dianilides (5) and (6).

(7) and (8) The phosphonyl dichloride sublimed at the m. p. It resembled camphor in appearance and odour. The dianilides were identical (mixed m. p.).

(9) Yield calc. on cetyl chloride. The constitution as *sec.*-derivative is assumed by analogy. The dianilide, free acid, and aniline salt were all pasty solids which could not be recrystallised.

(10) Yield calc. on cyclohexyl chloride. Clayton and Jensen (*J. Amer. Chem. Soc.*, 1948, **70**, 3880) give for the dichloride, b. p. 127.5—128.2°/15—16 mm. and m. p. 37—37.5°. Soborovski *et al.* (*Dokl. Akad. Nauk. U.S.S.R.*, 1949, **67**, 293) give 93—94°/1 mm. and m. p. 39—40°.

(11) Yield calc. on benzyl chloride.

(12) Procedure D led to a rise in temperature and complete solution of the aluminium chloride but no product was obtained on hydrolysis. Direct esterification of this solution also failed to give a product. The dianilide was identical with that from (18).

(13) The dianilide was identical (mixed m. p.) with that obtained by treating diisopropyl allylphosphonate successively with thionyl chloride and aniline. The ester was obtained from allyl bromide *via* the Arbusov rearrangement (Ford-Moore, unpublished).

(14) The reaction conditions described were the minimum which produced a reasonable yield. By A (1 week) the yield was nil, by E (24 hours) 18%, and by D (4 hours) 36%. The anilide was an amorphous solid which was purified as far as possible by rubbing it with light petroleum. The acid, produced by treatment of the dichloride with water, was hygroscopic.

(16) The aluminium chloride complex, recrystallised from methylene chloride, had m. p. 105—108°. A repetition of the preparation with 0.5 mol. of aluminium chloride gave a complex, m. p. 107° (decomp.), but differing in being much more soluble in methylene chloride. Numerous attempts to prepare a dianilide led only to trianilinophosphine oxide, m. p. 216—217°, identical with a specimen prepared from phosphorus oxychloride.

(17) The trianilide was prepared by heating the product with aniline, and the dianilide by treatment in the cold. Kabachnik *et al.* give dianilide, m. p. 169—170° (*Bull. Acad. Sci. U.R.S.S., Classe Sci. Chim.*, 1947, 97).

(20) and (21) Increased reaction time decreased the yield of dichloride. Aniline derivatives could not be made.

(22) The constitution is assumed by analogy. No material with b. p. higher than 123°/1 mm. was present.

(23) The dianilide was identical with that from (15).

(24) The anilide was identical (mixed m. p.) with that from (16).

(25) The dianilide was identical (mixed m. p.) with that from (17).

(26) The yield was good, but cannot be quoted as most of the product was lost. The product, purified by vacuum-sublimation, contained no fluorine. A crystalline aniline derivative could not be prepared.

(27) and (28) The aniline salt was identical (mixed m. p.) with that from (14).

(29) The product was identical (mixed m. p.) with that from (16).

(30) and (31) The dianilides were identical (mixed m. p.) with that from (2).

(32) When the reaction product was hydrolysed in the usual way, no product was isolated. By direct esterification of the complex a 75% yield of ethyl diethylphosphinate was obtained.

(33) Phosphorus but no chlorine was present. The product may be ethylisopropylphosphinic anhydride ($C_{10}H_{24}O_3P_2$ requires C, 47.2; H, 9.45%).

(34) No product was obtained by treatment with water. By direct esterification of the complex, ethyl ethylphosphonate was obtained.

(35) The dianilide was identical (mixed m. p.) with that from (3).

(36) The dianilide was identical (mixed m. p.) with that from (7).

and the alkyl chloride run slowly into the heated mixture. Excess of phosphorus trichloride was recovered by distillation. Temperatures and period of addition were as indicated.

D. The reagents were mixed, and heated in a sealed vessel at 100° for the period indicated.

E. The reagents were mixed and heated under reflux for the period indicated.

F. Aluminium chloride was suspended in phosphorus trichloride, and the gaseous alkyl halide passed slowly through the heated mixture. Excess of phosphorus trichloride was recovered by distillation.

Isolation of Phosphonyl Chloride.—Hydrolysis of aluminium chloride complexes, except in experiment 3, was accomplished as follows. The complex was dissolved in methylene chloride (about 5—10 volumes) and the solution cooled to about -20° by the addition of solid carbon dioxide. Water was then added in small portions with vigorous shaking until the milky suspension at first formed suddenly coagulated. The quantity of water required is recorded in the Table. The solution was rapidly filtered, the solvent driven off on a water-bath, and the residue distilled or allowed to crystallise.

Characterisation of Phosphonyl Compounds.—The dichloride was warmed with an excess of aniline and the product dissolved in benzene and washed with dilute hydrochloric acid. After evaporation to dryness the residue was recrystallised, usually from aqueous alcohol, but sometimes from benzene-chloroform.

Esterification of Complexes.—The complex (*e.g.*, from experiment 2) in methylene chloride (500 ml.) was cooled with solid carbon dioxide to about -20° . Absolute ethyl alcohol was then added cautiously until the vigorous reaction had subsided. The solution was then treated with small quantities of water until the milky suspension first formed suddenly coagulated, then filtered, and the filtrate was fractionated.

The Table contains only experiments from which identifiable phosphonyl dichlorides (or corresponding derivatives) were isolated. The following are some experiments from which identified phosphonyl derivatives were not obtained.

s-Tetrachloroethane. Procedure D (24 hours) with equimolecular proportions was used. On hydrolysis, apart from unchanged tetrachloride, only a very small amount of a substance, b. p. 58—80°/1 mm., was obtained.

Pentachloroethane. Procedure E (4 hours) and molecular proportions C_2HCl_5 0.25, PCl_3 0.25, and $AlCl_3$ 0.5 were used. On hydrolysis and after evaporation of solvent, phosphorus oxychloride (12.5 g.), unchanged pentachloride (3.5 g.), and a substance, b. p. 83—92°/3 mm. (17 g.), were obtained. Redistillation of the last did not lead to any product of constant b. p. (Found: C, 9.6; H, 0.7; hydrolysable Cl, 25.5. Calc. for C_2HOCl_5P : C, 8.4; H, 0.35; hydrolysable Cl, 24.9%). A crystalline derivative could not be obtained.

Hexachloroethane. Procedure D (24 hours) with mol. proportions C_2Cl_6 0.25, PCl_3 0.5, and $AlCl_3$ 0.5 was used. On hydrolysis unchanged hexachloride (30 g.) and phosphorus oxychloride (30 g.) were obtained.

Tetrachloroethylene. Procedure E (24 hours) with mol. proportions C_2Cl_4 0.25, PCl_3 0.25, and $AlCl_3$ 0.5 was used. On hydrolysis only phosphorus oxychloride (20 g.) was isolated.

Chlorotrifluoromethane. Procedure F. After 6 hours no change in the appearance of the reagents had occurred and no product was isolated after hydrolysis.

Attempted Preparation of Bisphosphonyl Derivatives.—(i) 1-Chloroethylphosphonyl dichloride (0.12 mol.) was refluxed for 10 hours with phosphorus trichloride (0.25 mol.) and aluminium chloride (0.25 mol.) after which all solid had disappeared. On hydrolysis only unchanged starting material (12 g.; b. p. 57—61°/4 mm.) was obtained. (ii) Ethylene dichloride (0.5 mol.) was refluxed for 24 hours with phosphorus trichloride (1.2 mols.) and aluminium chloride (2.0 mols.), all of which went into solution. On hydrolysis no material with b. p. above 79°/3 mm. was obtained (b. p. of $C_2H_4Cl \cdot POCl_2$ is 77°/6 mm.).

Reaction between Ethers and Phosphorus Trichloride.—(i) Diethyl ether (0.25 mol.) was added to a mixture of phosphorus trichloride (0.5 mol.) and aluminium chloride (0.5 mol.), all reagents being first cooled to 0°. When the initial vigorous reaction had died down, the mixture was heated to 100° in a sealed tube for 7 hours; all solid had disappeared. The white crystals to which the product set on cooling were dissolved in methylene chloride and hydrolysed (6 mols. of water). After filtration and distillation, 28 g. (0.19 mol.) of ethylphosphonyl dichloride were obtained. (ii) 2:2'-Dichlorodiethyl ether (0.25 mol.) in a similar way gave 23 g. (0.13 mol.) of 2-chloroethylphosphonyl dichloride (Found: C, 13.6; H, 2.4. Calc. for $C_2H_4OCl_2P$: C, 13.2; H, 2.2%) together with some unchanged ether. The trianilide was identical (mixed m. p.) with that from Expt. 17. (iii) Di-*n*-butyl ether (0.25 mol.) similarly gave 34 g. (0.21 mol.) of *sec*.-butylphosphonyl dichloride, b. p. 61°/3 mm., the dianilide, m. p. 150°, being identical

with that from Expts. 5 and 6. In addition there were 20 g. of material, b. p. 62—120°/3 mm., which was not identified.

Aluminium Chloride Complex from Ethyldichlorophosphine.—Equimolecular proportions of ethyldichlorophosphine and aluminium chloride reacted vigorously to give a liquid product. Chlorine passed into this was absorbed readily. When absorption ceased all the chlorine was removed by passing carbon dioxide through the liquid. On cooling, a solid mass was obtained which crystallised from methylene chloride in cubic crystals, m. p. 199—245°. A similar substance was obtained by mixing, in equimolecular proportions, ethylphosphorus tetrachloride and aluminium chloride. The complex from Expt. 2, when recrystallised from methylene chloride formed needles, m. p. 201—235°. The two complexes when mixed had m. p. 150—210°, but moisture was probably absorbed during manipulation. The cubic crystals (28.7 g), when hydrolysed in the usual way, gave 10.5 g. (83%) of ethylphosphonyl dichloride, b. p. 40°/2 mm. (identified as the dianilide).

Action of Alkyl Chloride on the Complexes.—The complex from Expt. 2 (35 g.) was heated under reflux for 24 hours with *n*-propyl chloride. On hydrolysis, 12.5 g. (81%) of ethylphosphonyl dichloride, b. p. 40°/2 mm. (identified as dianilide), were obtained with no trace of higher-boiling material. The complex with boiling carbon tetrachloride gave 83% of ethylphosphonyl dichloride with no trace of higher-boiling material.

Action of Hydrogen Sulphide on Complexes.—(a) Crystalline ethyl chloride-phosphorus trichloride-aluminium chloride complex (63 g., 0.19 mol.) was loosely packed in a vertical glass tube into the bottom of which hydrogen sulphide was introduced in a slow stream, the tube being kept at 90—100°. After 200 hours no more hydrogen chloride was evolved. The liquid residue was dissolved in methylene chloride and decomposed with water (35 ml.). After filtration and removal of the solvent a solid residue of dithiophosphoethane (20 g., 85%) was obtained which crystallised from carbon tetrachloride in glistening plates, m. p. 157° (Found : C, 20.0; H, 4.1. $C_2H_5S_2P$ requires C, 19.4; H, 4.05%). When this was warmed with water some went into solution with evolution of hydrogen sulphide. The residue on recrystallisation from light petroleum had m. p. 54—55° and was identified as thiophosphoethane (Found : C, 22.4; H, 4.9; S, 30.0. C_2H_5OSP requires C, 22.2; H, 4.7; S, 29.7%). The solution on evaporation gave a small quantity of hygroscopic solid, which after drying (P_2O_5) had m. p. 55—56° [the m. p. of ethylphosphoric acid is given by Kosolapoff (*J. Amer. Chem. Soc.*, 1945, 67, 1180) as 61—62°]. Thiophosphoethane did not appear to be appreciably decomposed by prolonged boiling in water.

(b) The crystalline complex (75 g., 0.22 mol.) was treated for 7 hours with hydrogen sulphide. The partly liquid product when hydrolysed (50 ml. water) in the usual way yielded thiophosphoethane (11.5 g., 47%) and ethylthiophosphonyl dichloride (13 g., 32%) (Found : C, 14.7; H, 3.1; Cl by hydrolysis, 44.2. Calc. for $C_2H_5Cl_2SP$: C, 14.7; H, 3.0; Cl, 43.5%), b. p. 54°/4 mm. Guichard (*Ber.*, 1899, 32, 1572) gives b. p. 80—82°/50 mm. The dianilide had m. p. 112—114° (Found : C, 59.1; H, 6.4. $C_{14}H_{17}N_2SP$ requires C, 60.9; H, 6.2%). Ford-Moore (unpublished) gave the m. p. of the dianilide obtained from the dichloride, prepared by a modification of Guichard's method, as 114°. Repetitions of this experiment with variations in temperature and time of passage invariably yielded a mixture of thio- and dithio-phosphoethane and the dichloride, with the last as the minor constituent.

(c) The crystalline complex (90 g., 0.27 mol.) was treated with hydrogen sulphide at 130° until reaction had ceased. The residue was dissolved in methylene chloride. One half of this solution, on decomposition with concentrated hydrochloric acid, filtration, and evaporation, gave a residue of practically pure dithiophosphoethane (14.5 g., 63%). The other half was shaken with 50 ml. of ethyl alcohol, and the solvent and excess of alcohol were distilled off. The residue was dissolved in methylene chloride, decomposed with water, filtered, and distilled. *O-Ethyl hydrogen ethyldithiophosphonate*, b. p. 85°/1 mm. (12.6 g., 40%), was thus obtained (Found : C, 27.8; H, 6.6. $C_4H_{11}OS_2P$ requires C, 28.2; H, 6.5%).

(d) The crystalline methyl chloride complex (71 g., 0.22 mol.) was treated at 130° with a stream of hydrogen sulphide until after 100 hours no more hydrogen chloride was evolved. The residue, which solidified on cooling, was dissolved in methylene chloride and decomposed with water (40 ml.). On evaporation a solid residue was obtained, having m. p. 197—200°, not improved after sublimation *in vacuo*. This proved to be thiophosphomethane (20 g., 98%) (Found : C, 12.8; H, 3.2. CH_3OSP requires C, 12.8; H, 3.2%).

Electrolysis of Ethyl Chloride-Phosphorus Trichloride-Aluminium Chloride Complex.—(i) The complex was dissolved in methylene chloride and a current passed through it. Aluminium chloride was precipitated at the anode. The liquid at the cathode smelled strongly of phos-

phines, but only a very small quantity of a substance, b. p. 35—85°/5 mm., which, by the formation of the dianilide, was shown to contain ethylphosphonyl dichloride, could be isolated. (ii) The complex (100 g., 0.29 mol.) was dissolved in methylene dichloride (200 ml.) and placed in an apparatus consisting of a porous pot fitted with a reflux condenser and a silver cathode dipping into a glass vessel with reflux condenser and platinum anode. The apparatus was cooled in solid carbon dioxide. The electrodes were connected across the 220-v DC mains. Current flowed at 1.15 amp., falling slowly to 0.5 amp. after 5 hours and to 0.2 amp. after a further hour. Whilst electrolysis proceeded a slow stream of chlorine was passed into the cathode compartment. Anhydrous aluminium chloride (20.7 g., 55%) was recovered from the anode compartment. From the cathode were obtained 50 g. of a white solid with an odour resembling that of camphor (Found: hydrolysable Cl, 49.3%). It reacted readily with sulphur dioxide to give a liquid from which thionyl chloride was recovered, together with a high-boiling material which solidified on cooling. The latter had an indefinite m. p., contained inorganic matter, and was not identified.

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