the mixture refluxed gently and it was subsequently allowed to attain room temperature over a 1-hr period. Dimethylchlorophosphine[15] (7.5 g, 0.09 mol) in 50 ml of anhydrous ether was then slowly added to the solution, the temperature being maintained at 0–5°. After the addition of water the organic layer was separated, dried, and fractionally distilled (0.2 mm). A forerun of 3.4 g of material boiling at 45–50° (phenyldimethylarsine) was rejected; the product (15.0 g; bp 80–81°) was analytically and spectroscopically (pmr) pure. *Anal.* Calcd for $C_{10}H_{16}AsP$: C, 49.6; H, 6.6. Found: C, 49.2; H, 6.5. Pmr spectrum: singlet τ 8.97, doublet (center τ 8.95; $J_{CH_3-P} = 4$ Hz).

Reaction of the product with sodium in liquid ammonia following the method given for Ic above gave a product which after fractional distillation was shown (nmr) to contain both P–H and As–H bonds. Other separation techniques (*e.g.*, spinning-band column) were not attempted.

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The Reaction of Tertiary Phosphines with Dichloramines

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The reactions of trisubstituted phosphines with chloramine,[1,2] methylchloramine,[2] and dimethylchloramine[3-5] had been previously reported from this laboratory, but the reactions of *N,N*-dichloroalkylamines with trisubstituted phosphines have not yet been reported. We decided to look into these reactions, in order not only to synthesize new compounds but also to compare the action of dichloramines on tertiary phosphines with the corresponding action of compounds containing P–Cl bonds.[6,7]

It was found, in the cases studied here, that the principal products of reactions of dichloramines with tertiary phosphines are the respective *N*-chloro-*N*-alkylaminotriphenylphosphonium chlorides, and no compounds containing nitrogen–nitrogen bonds were formed.

Experimental Section

Materials.—Triphenylphosphine was obtained from Aldrich Chemical Co. and checked for purity by its melting point and comparison of its infrared spectrum with that of a known sample.[8] Tributylphosphine was obtained from Peninsular ChemResearch and distilled before use, the fraction boiling at 125–130° (21 mm) being retained; lit.[9] bp 149.5° (50 mm). Coleman's method[10] was used to prepare dry diethyl ether solutions of *N,N*-dichloromethylamine and *N,N*-dichloroethylamine; these solutions were stored in a refrigerator over Linde Molecular Sieve 4A prior to use. The molarities of the solutions were determined by adding aliquot portions of the solutions to acidified potassium iodide solution and titration of the iodine released with standard sodium thiosulfate solution. Solutions of both dichloramines showed the strong absorption at 3100 Å (ϵ 370–375) known[11] to be characteristic of dichloramines.

All solvents were dried over calcium hydride or distilled and stored over Linde Molecular Sieve 4A until used.

Apparatus.—Manipulations of reactants and products were performed in an inert-atmosphere box (Vacuum Atmospheres Corp. Dri-Train HE-93B), and reactions were run under a dry nitrogen flush; such precautions were necessitated by the hygroscopic nature of the products of reaction. Ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer; nmr spectra were taken with a Varian A-60A spectrometer; infrared spectra were measured on Beckman IR-10 spectrometer.

Analyses.—With the exception of chloride analyses, analytical data were obtained by the Galbraith Microanalytical Laboratory. Chloride analyses were performed in this laboratory using the Volhard method, after the compounds had been hydrolyzed in sodium hydroxide solution and any resulting oxidizing species had been reduced with SO_2.

Formation of *N*-Chloro-*N*-methylaminotriphenylphosphonium Chloride.—In a 250-ml round-bottom flask was placed 8.87 g (33.8 mmol) of triphenylphosphine, along with 50 ml of dry diethyl ether and a magnetic stirbar. The flask was capped witn a pressure-equalizing funnel, and a flow of dry nitrogen was maintained while 154 ml of 0.22 *M* diethyl ether solution of *N,N*-dichloromethylamine (33.9 mmol) was added over a 0.5-hr period. Stirring was maintained throughout the addition, as was external cooling by means of an ice bath. The reaction mixture containing a white solid, which immediately began to form in the reactant vessel, was stirred an additional 15 min; the solid was then removed by filtration in the drybox and was pumped dry (yield 8.03 g, 74.9% of the theoretical weight of $[(C_6H_5)_3PNClCH_3]Cl$ based on the triphenylphosphine used). The reaction solution was titrated for residual oxidizing capacity and a titer corresponding to 4.17 mmol of unreacted *N,N*-dichloromethylamine was found. The solid was dissolved in the minimum amount of chloroform and reprecipitated by the addition of dry diethyl ether;[12] mp 145–149° dec. *Anal.* Calcd for $[(C_6H_5)_3PNClCH_3]Cl$: N, 3.87; Cl, 19.58; P, 8.55; C, 63.00; H, 5.01. Found: N, 3.62; Cl, 19.4; P, 9.11; C, 63.22, H, 5.74. The infrared and nmr spectra of the solid are given in Tables I and II. In spite of the somewhat less than satisfactory hydrogen analysis, the evidence overwhelmingly supports the formula assigned. The reaction was repeated three times with substantially the same results.

Formation of *N*-Chloro-*N*-ethylaminophosphonium Chloride.—This synthesis was carried out in a manner analogous to the previous example using 7.55 g of triphenylphosphine (28.8 mmol) in 50 ml of diethyl ether and 102 ml of a 0.283 *M* diethyl ether solution of *N,N*-dichloroethylamine (28.8 mmol). The solid product, which weighed 9.85 g (90.9% of the theoretical weight of $[(C_6H_5)_3PNClC_2H_5]Cl$ based on triphenylphosphine) was filtered off and recrystallized as above; mp 184–185° dec. *Anal.* Calcd for $[(C_6H_5)_3PNClC_2H_5]Cl$: N, 3.72; Cl, 18.85; P, 8.23. Found: N, 4.01; Cl, 19.1; P, 9.11. There was 2.0 mmol of unreacted *N,N*-dichloroethylamine found in the reaction liquor. The infrared and nmr spectra of the solid are given in Tables I and II.

Reaction of Tributylphosphine with *N,N*-Dichloromethylamine.—A solution of 7.63 g (37.8 mmol) of tributylphosphine in 50 ml of dry ether and 49 ml of 0.76 *M* *N,N*-dichloromethylamine (37.2 mmol) were mixed according to the procedure described above. The solution clouded immediately and a colorless oil separated. We were unable to bring about the crystallization

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[12] It should be noted that if recrystallization is attempted by this method, the solid exhibits an extreme tendency to form oils. Repeated washings with ether will usually result in crystallization, however.

TABLE I

INFRARED SPECTRA OF COMPOUNDS (CM^{-1})[a]

$[(C_6H_5)_3PNClCH_3]Cl$

3100–2800 vs, b, 2710 s, b, 2330 w, 2220 w, 1980 m, b, 1920 w, 1830 m, 1680 w, 1580 m, 1380 w, 1260 b, s, 1250 b, m, 1175 w, 1168 w, 1105 s, b, 987 w, 868 m, 683 w, 612 m, 544 s, 532 s, 522 sh, 494 s, 457 w

$[(C_6H_5)_3PNClC_2H_5]Cl$

3100–2500 vs, vb, 1940 w, b, 1900 w, b, 1583 m, 1485 w, 1430 s, 1195 m, 1115 s, 1080 w, 998 m, 978 m, 875 w, 797 w, 767 m, 727 s, 698 s, 548 s, 525 s, 500 m, 465 w

[a] Key: s, strong; m, medium; w, weak; sh, shoulder; v, very; b, broad.

TABLE II

NUCLEAR MAGNETIC RESONANCE PROPERTIES OF *N*-CHLORO-*N*-ALKYLAMINOTRIPHENYLPHOSPHONIUM CHLORIDES[a]

Compound	τ	*J*, cps
$[(C_6H_5)_3PNClCH_3]Cl$	2.0–2.8, complex multiplet (phenyl)	. . .
	7.23, doublet (NCH_3)	12.8
$[(C_6H_5)_3PNClC_2H_5]Cl$	2.0–2.6, complex multiplet (phenyl)	. . .
	6.87, octet (NCH_2–)	17.5 ($PNCH_2$–) 7.2 (NCH_2CH_3)
	8.75, triplet (–CH_3)	7.2

[a] All spectra in $CDCl_3$; tetramethylsilane internal standard.

of the oil. The oil was treated to form a Reinecke's salt derivative;[6,13] mp 122–123° dec. Its infrared spectrum matched that of an authentic sample of $(C_4H_9)_3PO \cdot H[Cr(SCN)_4(NH_3)_2]$, mp 121–123° dec, lit.[13] mp 124–126°, and a mixture of the known compound $(C_4H_9)_3PO \cdot H[Cr(SCN)_4(NH_3)_2]$ with the Reinecke's salt derivative from our oil showed a melting point of 122–123° dec.

Discussion

The elementary analyses, the spectral data listed in Table I, the mode of formation of the substances, and the stoichiometry of the reactions all lead us to conclude that we have isolated and identified members of a new series of compounds, the *N*-chloro-*N*-alkylaminotriphenylphosphonium chlorides. The reasonably conceivable reactions of dichloramines with tertiary phosphorus are

$$2(C_6H_5)_3P + NRCl_2 \longrightarrow [((C_6H_5)_3P)_2NR]Cl_2 \qquad (1)$$

$$2(C_6H_5)_3P + NRCl_2 \longrightarrow (C_6H_5)_3PNR + (C_6H_5)_3PCl_2 \qquad (2)$$

$$2(C_6H_5)_3P + 2NRCl_2 \longrightarrow 2(C_6H_5)_3PCl_2 + N_2R_2 \qquad (3)$$

$$(C_6H_5)_3P + NRCl_2 \longrightarrow [(C_6H_5)_3PNClR]Cl \qquad (4)$$

Reaction 1 may be ruled out on the basis of the stoichiometry found (1:1 triphenylphosphine–dichloramine), nmr data (the product in (1) would show a triplet when R = CH_3), and elemental analysis. Reaction 2 is unlikely because of the stoichiometry we have found, the elemental analyses, and the absence of a characteristic P=N stretch in the infrared spectrum in the 1385–1325-cm^{-1} region.[14,15] Reaction 3, while of the proper stoichiometry, is unacceptable not only because of elemental analysis and nmr data but also because of the fact that no evolution of gases was detected during the course of the reactions; N_2R_2, which decomposes to nitrogen gas at the temperatures employed here, would be easily detected in this way. Only reaction 4 can satisfactorily explain all the observations made.

The nmr data for the compounds reported here are interesting. The methyl group in CH_3NCl_2 shows a singlet (CCl_4, TMS internal) at τ 6.36. The methyl group in *N*-chloro-*N*-methylaminotriphenylphosphonium chloride exhibits a doublet centered at τ 7.23. The replacement of a Cl in a dichloramine by a R_3P group lessens electron withdrawal from the group attached to the nitrogen atom. It is possible that the change in electronegativity when PR_3 replaces Cl is in part offset by the possibility of $p\pi$–$d\pi$ bonding in aminophosphonium compounds.

The compounds exhibit the properties one would expect of them. They hydrolyze rapidly producing $(C_6H_5)_3PO$, mp 152–153°, lit.[16] mp 152–153°. They react slowly with an acidified solution of potassium iodide, in contrast with the almost instantaneous reactions of chloramines with acidic potassium iodide solutions. They are soluble in polar solvents (water, chloroform, methylene chloride, ethanol, acetone, methanol) and insoluble in less polar solvents (diethyl ether, benzene, ligroin). Interestingly, it appears that the N–Cl bond may be more susceptible to hydrolysis than the P–N bond. In an attempt to form the hexafluorophosphate derivative of *N*-chloro-*N*-methylaminotriphenylphosphonium ion, a saturated aqueous solution of potassium hexafluorophosphate was added to a solution of the phosphonium species. The nmr spectrum of the resulting solid showed two methyl resonances (both doublets; τ 7.21, $J_{\text{PNCH}} = 13.8$ Hz; τ 7.30, $J_{\text{PNCH}} = 13.0$ Hz) and a new, broad peak at τ 3.05. Presumably, this solid was a mixture of $[(C_6H_5)_3PNClCH_3]PF_6$ and $[(C_6H_5)_3PNHCH_3]PF_6$. A strong infrared absorption was observed for all compounds near 1120 cm^{-1}, characteristic of phenyl-substituted tetracoordinate phosphorus.[17]

The product of the reaction between tributylphosphine and *N*,*N*-dichloromethylamine remains incompletely characterized, although its spectral behavior is very similar to that of the *N*-chloro-*N*-methylaminotriphenylphosphonium chloride prepared above, and its nmr spectrum exhibits a doublet at τ 7.31, $J_{\text{PNCH}} =$ 13.0 Hz; this is due presumably to the –$NClCH_3$ protons. It easily forms the Reinecke's salt derivative, as one expects an aminophosphonium species to do after hydrolysis to R_3PO.

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