

state, with metallic radii much too large for the formation of one of the above structures.

In Table VI, bond lengths between the atoms in the Mn_5Si_3 -type lattices are listed. The shortest distance between the metals is in the 4d position. Taking half these distances, one gets values equal to the covalent radii of these metals. On the other hand, the bond length between the metals in the 6g position equals the length known in the metallic state. It can therefore be concluded that the metal-metal bond in the lattice is of two different types, covalent in the c direction (4d), and of a metallic character in the layers normal to the c axis (6g).

Carbon atoms occupy the 0, 0, 0 and 0, 0, $1/2$ positions in the lattice and so are located in octahedral holes formed by the 6g metals. Table VII lists the diameters of the octahedral holes in the Mn_5Si_3 -type lattice for the various binary compounds, as well as for the compounds containing carbon. The third column contains the effective radii of carbon in the ternary phases. The diameter of the octahedral holes (D) was calculated by the expression

$$D = r_{oct} - r_{M_{6g}}$$

where r_{oct} is the diagonal length between two metals in neighboring layers ($\sqrt{(1 - 2x_M)^2c^2 + (0.5x)^2a^2}$), and $r_{M_{6g}}$ is the metal-metal distance in the 6g position ($1.732ax_M$).

From the values shown in Table VII it can be seen that the diameter of the octahedral holes decreases toward the heavier rare earth elements and that the effective radii of carbon (actually half the diameter of the octahedral hole) in these compounds have values falling between the values of the covalent radius (0.77 \AA^{19}) and atomic radius (0.914 \AA^{20}) of carbon.

These facts explain the increase of cell constant c in

the ternary phases toward the heavier elements, this increase being necessary for the existence of octahedral holes with enough space for the location of the carbon atoms. Because of their size, the octahedral holes can accommodate one carbon atom only, in good agreement with our experimental results. According to the values of the estimated effective radii of the carbon, the bonds formed between the metals and carbon are essentially atomic with a slight covalent character.

TABLE VII
DIAMETERS OF THE OCTAHEDRAL HOLES (D) AND
RADI OF CARBON (R_C) IN VARIOUS
 Mn_5Si_3 -TYPE LATTICES

M	M_5Si_3	M_4Si_3C		M_6Ge_3	M_5Ge_3C	
	$D, \text{ \AA}$	$D, \text{ \AA}$	R_C	$D, \text{ \AA}$	$D, \text{ \AA}$	R_C
Ce	1.74	1.74	0.87
Pr	1.73	1.74	0.87
Nd	...	1.70	0.85	1.71	1.73	0.865
Sm	1.65	1.69	0.845	1.68	1.71	0.855
Gd	1.65	1.67	0.835	1.66	1.67	0.835
Tb	1.64	1.63	0.815	1.64	1.66	0.83
Dy	1.62	1.65	0.825	1.63	1.66	0.83
Ho	1.61	1.64	0.82	1.62	1.65	0.825
Er	1.60	1.63	0.185	1.61	1.65	0.825
Tm	1.60	1.62	0.81	1.60	1.64	0.82
Yb	1.62	1.62	0.81
Lu	1.57	1.58	0.79	1.59	1.62	0.81
Y	1.63	1.66	0.83	1.64	1.67	0.835

Stabilization of the hexagonal structure was obtained in the case of Nd_5Si_3 by filling the octahedral holes with carbon. In view of the ratio R_M/R_{Si} , Nd_5Si_3 would not crystallize in the Mn_5Si_3 -type structure, but the addition of carbon in the octahedral holes and formation of Nd_5C bonds caused an energy gain, thus stabilizing the hexagonal phase.

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The Chloramination of Some Ditertiary Phosphines and Arsines

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The reactions of various phenyl-substituted ditertiary phosphines and arsines with chloramine have been shown to result in the formation of double-chloramination products in the presence of ammonia. In some cases, monochloramination products could be isolated using ammonia-free chloramine. The new compounds obtained have been characterized by their elemental analyses and infrared and proton magnetic resonance spectra.

Introduction

It has been well established that chloramine reacts with tertiary phosphines or arsines to form amino-phosphonium or aminoarsonium chlorides.¹⁻⁴ Apart

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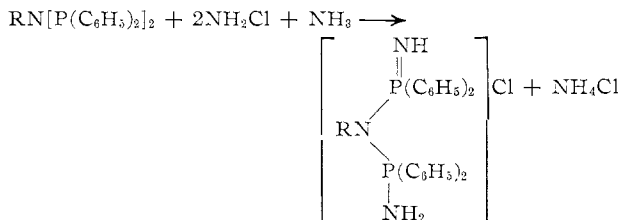
from the simple tertiary phosphines, reactions of chloramine with systems containing more than one phosphorus atom and more than one basic site, *e.g.*, bis(diphenylphosphino)amines⁵ and bis(diphenylphosphino)hydrazines,^{6,7} have been studied and it has been shown that chloramination always occurs on the phos-

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phorus atoms in these systems. However, the reactions of chloramine with simple ditertiary phosphines or arsines have not been reported. It has further been shown that in the reactions of chloramine in the presence of ammonia with aminophosphines⁵ or hydrazinophosphines,⁶ having more than one phosphorus atom, dehydrohalogenation occurs, as shown by



However, if ammonia-free chloramine is used, a double-chloramination product which has not undergone dehydrohalogenation is obtained.⁷

The present investigation was undertaken to learn about the behavior of chloramine toward ditertiary phosphines and arsines. The results show that double-chloramination products are obtained in all cases studied, but that dehydrohalogenation does not occur, even when these reactions are carried out in the presence of ammonia.

Experimental Section

All operations were conducted in a nitrogen atmosphere in a Vacuum Atmosphere Model HE-43 Dri-Lab equipped with a Model HE-93 Dri-Train.

Materials.—Solvents used were dried over calcium hydride. 1,4-Bis(diphenylphosphino)benzene, mp 159–161°, was synthesized as reported earlier,⁸ the reported melting point being 166–168.5°. It was characterized by its elemental analysis, its proton magnetic resonance spectrum showing only phenyl proton resonances, and its infrared spectrum, which showed no absorption attributable to P–O at 1190 cm⁻¹. *Anal.* Calcd for (C₆H₅)₂PC₆H₄P(C₆H₅)₂: C, 80.70; H, 5.42. Found: C, 80.57; H, 5.33.

trans-1,2-Bis(diphenylphosphino)ethylene, mp 118–120°, was prepared by the method of Aguiar and Daigle,⁹ who reported its melting point to be 125–126°. The proton magnetic resonance and infrared spectra of this compound agreed very well with those reported by these authors. *trans*-1,2-Bis(diphenylarsino)ethylene, mp 96–97°, was prepared by a method analogous to that of Aguiar and Daigle,⁹ *i.e.*, by the reaction of *trans*-1,2-dichloroethylene on diphenyllithium arsenide in tetrahydrofuran. The proton magnetic resonance of this compound in CDCl₃ gave a singlet at τ 2.92 and a complex peak at τ 2.7 with an area ratio of 1:10. *Anal.* Calcd for (C₆H₅)₂AsCH=CHAs(C₆H₅)₂: C, 64.48; H, 4.58; As, 30.94. Found: C, 64.62; H, 4.52; As, 30.74. Other ditertiary phosphines and arsines used in this investigation were supplied by Alfa Inorganics Inc. and their purities were checked by examining their proton magnetic resonance spectra, which showed only the expected signals and compared well with those reported in the literature.^{10,11} The proton magnetic spectra of bis(diphenylarsino)methane and bis(diphenylarsino)ethane showed their bridge protons as singlets at τ 7.40 and 7.88, respectively, and phenyl proton resonances in the expected range.

Chloramine was prepared by the gas-phase chlorination of am-

monia as described earlier.¹² The rate of production of chloramine was 0.1 mol/hr. Etheral chloramine solutions were freed from ammonia and dehydrated by passing the solutions through anhydrous copper sulfate.¹³

Analyses and Ir and Nmr Spectra.—Elemental analyses were carried out by the Galbraith Microanalytical Laboratories. Analytical and melting point data are reported in Table I. The infrared spectra (Table II) were recorded with a Beckman Model IR-10 infrared spectrometer. The spectra of solids were taken in the form of pressed KBr pellets or in the form of Kel-F mulls for the range 2.5–7.5 μ and as Nujol mulls for the range 7.2–20 μ using KBr plates. The proton magnetic resonance spectra were recorded with a Varian A-60A spectrometer. The spectra of solids were run mostly in deuteriochloroform solutions with tetramethylsilane (TMS) as the internal standard.

Procedure for Chloramination Reactions.—The chloramination reactions were carried out in both the presence and the absence of ammonia. Illustrations of each of the experimental procedures are described below.

Method A. Chloramination of Bis(diphenylphosphino)methane in the Presence of Ammonia.—The mixture of chloramine and excess ammonia obtained by the chloramine generator¹² was passed into a solution of bis(diphenylphosphino)methane (2.6 g, 6.5 mmol) in 50 ml of benzene for 0.5 hr (approximately 0.05 mol of chloramine). A white precipitate formed immediately. The reaction mixture was allowed to remain at room temperature overnight to expel excess ammonia through a guard tube containing Drierite. The solid reaction products were removed by filtration, separated from ammonium chloride by extraction with chloroform, and recovered by adding the chloroform solution to an excess of dry ether. The yield was 1.8 g (55% of theory).

Method B. Chloramination of Bis(diphenylarsino)methane with Ammonia-Free Chloramine.—In a typical experiment, 50 ml of an ammonia-free solution of chloramine in ether (0.1 *m*) was added dropwise to a solution of bis(diphenylarsino)methane (1.1 g, 2.3 mmol) in 40 ml of ether. The reaction occurred immediately with the formation of a white precipitate. This solid was recovered by filtration in a drybox after the reaction mixture had been stirred for 4 hr. The solid residue was washed with ether and dried under vacuum. The yield was 1.3 g (97% of theory).

Method C. Chloramination of *trans*-1,2-Bis(diphenylphosphino)ethylene with Ammonia-Free Chloramine in the Vacuum Line.—An etheral solution of anhydrous, ammonia free chloramine was taken into a flask and connected to the vacuum line. The solution was transferred to a graduated tube attached to the vacuum line and degassed; a 1-ml sample was taken out to measure the concentration of the chloramine solution. The remaining solution contained 11.2 mmol of chloramine. This solution was again degassed and transferred completely onto a degassed solution of *trans*-1,2-bis(diphenylphosphino)ethylene (0.56 g, 1.4 mmol) in 20 ml of dry benzene cooled to liquid nitrogen temperature. The temperature of the mixture was slowly raised to room temperature. The mixture was stirred overnight and then the volatile materials were distilled out. The remaining solid was extracted with chloroform and reprecipitated by adding excess ether. The total yield of the recrystallized material was 0.3 g (48% of theory).

The reaction of 1,4-bis(diphenylphosphino)benzene and chloramine in the presence of ammonia gave a mixture of products. The solids obtained were extracted on a Soxhlet extractor with acetonitrile for 12 hr. On the addition of diethyl ether to the acetonitrile solution, a white solid precipitated; it was filtered and dried under vacuum. This was shown by its melting point and infrared spectrum to be the monochloramination product. The remaining residue in the thimble was fractionally crystallized several times from a mixture of absolute ethanol and acetone

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TABLE I
 CHLORAMINATION REACTION PRODUCTS

Reactant	Solvent	Method	Product	Mp, °C	Analysis of products, %						
					C	H	N	P or As	Cl	Yield	
$(C_6H_5)_2PCH_2P(C_6H_5)_2$	C_6H_6	A	[[$(C_6H_5)_2PCH_2P(C_6H_5)_2$] Cl_2 (III)]	188–190	Calcd	61.59	5.38	5.75	12.72	14.56	55
					Found	62.10	5.09	6.04	12.83	14.40	
$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$	C_6H_6	A	[[$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$] Cl_2 (IV)]	262–265 dec	Calcd	62.28	5.63	5.59	12.36	14.15	45
					Found	62.37	5.87	5.59	12.20	14.27	
$(C_6H_5)_2AsCH_2As(C_6H_5)_2$	$(C_2H_5)_2O$	B	[[$(C_6H_5)_2AsCH_2As(C_6H_5)_2$] Cl_2 (V)]	175 dec	Calcd	52.20	4.56	4.87	26.05	12.32	97
					Found	49.86	5.01	4.36	26.06	12.65	
$(C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2$	$(C_2H_5)_2O$	B	[[$(C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2$] Cl_2 (VI)]	140 dec	Calcd	52.99	4.79	4.75	25.43	12.03	90
					Found	51.47	5.28	5.01	24.99	12.66	
$(C_6H_5)_2PC_6H_4P(C_6H_5)_2$	C_6H_6	B	[[$(C_6H_5)_2PC_6H_4P(C_6H_5)_2$] Cl (VII)]	135 dec	Calcd	72.36	5.26	2.81	12.44	7.12	60 ^a
					Found	72.38	5.20	2.99	12.12	7.44	
$(C_6H_5)_2PC_6H_4P(C_6H_5)_2$	C_6H_6	A	[[$(C_6H_5)_2PC_6H_4P(C_6H_5)_2$] Cl_2 (VIII)]	288–290	Calcd	65.58	5.14	5.10	11.27	12.90	46 ^b
					Found	63.81	5.49	5.42	10.94	13.25	
$(C_6H_5)_2PCH=CHP(C_6H_5)_2$	C_6H_6	C	[[$(C_6H_5)_2PCH=CHP(C_6H_5)_2$] Cl (IX)]	215–218	Calcd	69.72	5.40	3.13	13.88	7.91	48
					Found	69.70	5.30	2.75	13.50	7.40	
$(C_6H_5)_2PCH=CHP(C_6H_5)_2$	C_6H_6	A	$C_{26}H_{27}N_3P_2Cl_2$ (X)	140 dec	Calcd	60.71	5.29	8.17	12.04	13.78	42
					Found	61.20	5.13	7.96	12.12	10.54	

^a Yield obtained as in procedure B. ^b Compound VII was also recovered in 19% yield along with VIII.

(1:1 ratio by volume), giving a white powder (mp 288–290°) which was shown to be the double-chloramination product.

Results and Discussion

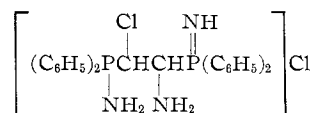
The results of the present investigation indicate, in general, the similarity between the reactions of chloramine with a tertiary phosphine and a ditertiary phosphine; however, the chloramination occurs at both phosphorus atoms when a ditertiary phosphine reacts with chloramine. This is demonstrated by the elemental analyses of the reaction products and their infrared spectra, which show a strong band at 1120 cm^{-1} in each case, corresponding to a phenyl group attached to a tetracoordinated phosphorus atom. The ³¹P nmr spectrum of [(C₆H₅)₂(NH₂)PCH₂P(NH₂)(C₆H₅)₂] Cl_2 in chloroform exhibits a single resonance at –22.0 ppm from the 85% phosphoric acid external standard. This indicates the equivalence of the two phosphorus atoms in this compound. Also, the ³¹P chemical shift in the nmr spectrum is of the same order as observed in the case of various other aminophosphonium chlorides.² The reactions of chloramine with ditertiary arsines are analogous to those of ditertiary phosphines. The infrared spectra of the doubly chloraminated arsonium compounds each show an intense band at 1085–1090 cm^{-1} , as observed in other phenyl-substituted arsonium chlorides.⁴

The reactions reported in this investigation are somewhat different from those of bis(diphenylphosphino)amines⁵ or -hydrazines⁶ with chloramine in the presence of ammonia, where dehydrohalogenated products are invariably obtained. This difference may be rationalized by the presence of an additional nitrogen atom connecting the two phosphorus atoms in the bis(diphenylphosphino)amines or -hydrazines. Thus, the electronegativity of the amino nitrogen atom on the phosphorus should increase through an inductive effect and favor the loss of a proton.

It is interesting to note that the sole product isolated

from the reaction of chloramine with 1,4-bis(diphenylphosphino)benzene in the absence of ammonia was the monochloramination product. Chloramination of this substance in the presence of ammonia, however, yields a mixture of the mono- and dichloramination products. Continued chloramination of this substance yields only the dichloramination product. In both the mono- and dichloramination products, amination occurs on the phosphorus atoms.

In the case of the reaction of ammonia-free chloramine with *trans*-1,2-bis-(diphenylphosphino)ethylene, monochloramination of one of the phosphorus atoms occurs, but the ethylenic double bond is unaffected. This is demonstrated by the strong band at 1120 cm^{-1} in the infrared spectrum; this band is characteristic of a phenyl-substituted tetracoordinate phosphorus atom. An analogous product is obtained from the reaction of *trans*-1,2-bis(diphenylarsino)ethylene with ammonia-free chloramine at reduced pressure. This product, however, could not be obtained pure. In the presence of ammonia, chloramine reacts with *trans*-1,2-bis(diphenylphosphino)ethylene to yield a product whose analysis is roughly represented by the formula C₂₆H₂₇N₃P₂Cl₂, which corresponds to trichloramination and monodehydrochlorination. The following structure which assumes addition of the third chloramine molecule across the ethylenic double bond is suggested, but at present can only be regarded as speculation.



Such addition across olefinic double bonds has recently been reported.¹⁴ The infrared spectrum of this compound does show a strong band at 1120 cm^{-1} . However, no band could be observed at 1250 cm^{-1} which could be attributed to the P=N bond.⁷

TABLE II
 INFRARED DATA (CM⁻¹)^a

(C ₆ H ₅) ₂ AsCH=CHAs(C ₆ H ₅) ₂	
3070 m, 3050 m, 1580 m, 1483 s, 1435 s, 1385 w, 1335 w, 1305 m, 1262 w, 1190 w, 1145 s, 1080 m, 1070 m, 1030 s, 1005 s, 990 s, 910 w, 850 w, 800 w, 740 vs, 700 vs, 610 s, 480 s, 470 s	
[(C ₆ H ₅) ₂ (NH ₂)PCH ₂ P(NH ₂)(C ₆ H ₅) ₂]Cl ₂	
3160 s, b, 3020 s, b, 2900 s, 1590 m, 1565 m, b, 1485 sh, 1480 m, 1435 vs, 1395 m, 1290 sh, 1260 s, 1230 s, 1180 w, 1160 w, 1120 vs, 1020 w, 1000 m, 960 s, 900 w, 820 s, 810 s, 750 s, 720 vs, 690 vs, 535 s, 515 s, 490 s, 475 m, 445 m	
[(C ₆ H ₅) ₂ (NH ₂)PCH ₂ CH ₂ P(NH ₂)(C ₆ H ₅) ₂]Cl ₂	
3150 m, b, 3040 s, b, 2900 s, 1590 w, 1485 w, 1440 vs, 1400 m, b, 1210 w, 1190 w, 1160 w, 1135 s, 1120 vs, 1000 m, 970 s, 800 m, 750 s, 730 vs, 690 s, 510 s, 500 s	
[(C ₆ H ₅) ₂ (NH ₂)AsCH ₂ As(NH ₂)(C ₆ H ₅) ₂]Cl ₂	
3140 m, b, 3050 m, b, 1480 w, 1440 s, 1410 vs, 1085 s, 1020 w, 1000 w, 990 s, b, 740 s, 690 s, 470 m, 455 m	
[(C ₆ H ₅) ₂ (NH ₂)AsCH ₂ CH ₂ As(NH ₂)(C ₆ H ₅) ₂]Cl ₂	
3140 s, b, 3050 s, b, 1485 m, 1440 s, 1410 vs, 1310 w, 1170 w, b, 1090 vs, 1025 w, 1000 m, 880 s, b, 745 s, 695 s, 600 w, 480 s, 455 m	
[(C ₆ H ₅) ₂ PC ₆ H ₄ P(NH ₂)(C ₆ H ₅) ₂]Cl	
3100-2820 s, b, 1595 m, 1490 m, 1445 s, 1385 w, 1310 w, 1190 m, b, 1120 vs, 1000 w, 970 w, 840 w, 820 w, 750 s, 725 vs, 695 vs, 570 s, 550 s	
[(C ₆ H ₅) ₂ (NH ₂)PC ₆ H ₄ P(NH ₂)(C ₆ H ₅) ₂]Cl ₂	
3180-2750 s, b, 1595 m, 1555 w, 1445 m, 1415 w, 1390 w, 1310 w, 1130 s, 1115 s, 1020 w, 995 m, 965 m, 950 m, 820 w, 750 vs, 725 vs, 700 s, 685 vs, 610 w, 560 vs, 540 s, 510 s, 490 m	
[(C ₆ H ₅) ₂ PCH=CHP(NH ₂)(C ₆ H ₅) ₂]Cl	
3100-2750 m, b, 1650 w, b, 1595 w, 1490 w, 1440 m, 1310 w, 1190 s, 1170 m, 1120 s, 1105 sh, 1070 w, 1020 m, 995 m, 850 w, 770 s, 742 s, 720 vs, 690 s, 530 vs, 500 s	

^a Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; b, broad; v, very.

The low solubilities of some of these compounds in suitable solvents prevented the determination of their detailed nmr spectra. Suspensions of compounds IV-VI (Table I) in CDCl₃ or DMSO-*d*₆ showed resonances in the phenyl region only. Compound III, sufficiently soluble in CDCl₃, exhibited resonances due to phenyl groups, a broad band due to -NH₂ groups at τ 3.9, and the rather unusual spectral behavior of protons on the bridging carbon atom. The methylene protons in this compound appear as two peaks resembling a "doublet" ($J = 6.0$ cps) at τ 4.72, whereas in bis(diphenylphosphino)methane, the >CH₂ protons

appear as a triplet ($J = 1.5$ cps) at τ 7.2. The doublet nature of the peak is difficult to understand. Similar results have been obtained by Brophy and Gallagher¹⁰ and Carty and Harris¹¹ in studies of the proton magnetic resonance spectra of some organophosphorus compounds similar to those studied in the present case. The derivatives of 1,4-bis(diphenylphosphino)benzene, VII and VIII, revealed only broad complex resonances in the phenyl region. No separate peak attributed to the -NH₂ group could be observed in the case of VII, whereas, there seems to be such a peak near the phenyl resonances in VIII; however, this peak cannot be assigned with certainty. These spectra compare well with that of [(C₆H₅)₃P(NH₂)]Cl,² where the -NH₂ peak was found to be very near the phenyl resonances, and it is quite likely that -NH₂ signals appear underneath the phenyl absorptions in the present cases. Whereas compound X decomposes in CDCl₃, the proton magnetic resonance spectrum of IX again showed resonances in the phenyl region only. The ethylene protons in *trans*-1,2-bis(phenylphosphino)ethylene appear as a triplet at τ 3.22. This triplet is very near the complex peak which is assigned to the phenyl protons at τ 2.7 in CDCl₃⁹ and which has been reported¹⁰ to appear at τ 2.04 in [(C₆H₅)₂P(CH₃)CH=CH(CH₃)P(C₆H₅)₂]I₂. It seems again quite plausible to assume that resonances due to both -CH=CH- and -NH₂ groups have been covered by the phenyl resonances.

The infrared spectra of the bis-phosphonium compounds show almost all of the expected major bands resulting from phenyl groups, in addition to the characteristic band at 1120 cm⁻¹ assigned to phenyl-substituted tetracoordinate phosphorus. Some of the more obvious bands are the C-H stretch in the 3000-cm⁻¹ region, a weak- to medium-intensity band at 1590 cm⁻¹ assigned to the phenyl "C=C" vibration, a strong band between 1450 and 1435 cm⁻¹ assigned to the phosphorus-phenyl vibration, and two strong absorptions assigned to C-H out-of-plane deformation near 750 and 690 cm⁻¹. Similarly, infrared spectra of the bis-arsonium compounds exhibit vibrations assigned to phenyl groups³ along with the characteristic strong band at 1025-1090 cm⁻¹ assigned to phenyl-substituted tetracoordinated arsenic.⁴

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