case, $C_3F_8P^+$ next lost a fragment of 88 amu, shown by mass measurement of the ion at m/e 131 to be CF_4

$$C_3F_8P^+ \longrightarrow CF_3PCF^+ + CF_4 \qquad (9)$$

This was surprising as the ion $C_3F_8As^+$, observed in the mass spectrum of the arsine, $(CF_3)_3As$, has been shown[2] to lose not CF_4 but AsF_3

$$C_3F_8As^+ \longrightarrow C_3F_5^+ + AsF_3 \qquad (10)$$

The most notable feature of the mass spectra of the trifluoromethylphosphines and -arsines is the occurrence of extensive rearrangement during fragmentation with transfer of fluorine from the fluoroalkyl group to the phosphorus or arsenic atom. Similar rearrangement processes have been observed in the mass spectra of the pentafluorophenyl derivatives of phosphorus and some group IV elements.[1] The rearrangement of F atoms is not observed in the mass spectra of trifluoromethylamines,[11] nor do alkyl- and arylphosphorus compounds exhibit rearrangement processes in which hydrogen atoms are transferred to the phosphorus atom.[12] The rearrangement process thus appears to be influenced by both the nature of the potential migrant atom and the nature of the accepting atom.

In a comprehensive study of inductive and resonance effects of fluoroalkyl and related groups substituted on the phenyl ring, Sheppard[13] suggested that interaction of the nonbonding p orbitals of the F atom in the CF_3 group with the aromatic π electrons of the phenyl ring was the most reasonable source of the unusual substituent effects of the CF_3 group. We propose that the rearrangement processes observed in the mass spectra of the trifluoromethylphosphines arise because of the interaction of the fluorine p orbitals with the unoccupied d orbitals of the phosphorus atom. The lack of similar rearrangements in the trifluoromethylamines[11] is therefore a consequence of the lack of appropriate orbitals on nitrogen for interaction.

If we assume bond lengths of 1.90 and 1.33 A for P–C and C–F (taken from the crystal structures of P–CF_3 pentamer and tetramer[14]) and normal tetrahedral angles around P and within the CF_3 group, then the smallest F–P separation is 2.7–2.8 A, about 15% larger than the value of 2.36 A for the F–C (ring) separation estimated by Sheppard[13] in benzotrifluoride but well within the sum of the F and P van der Waals radii of 3.25 A. Any enlargement of the CF_3–P–CF_3 angle by repulsions within the molecule or shrinkage of the P–C bond would reduce the F–P separation and increase the interaction between them.

It is interesting to note that the mass spectrum of benzotrifluoride[15] shows an intense ion ($C_6H_5F^+$) which must be formed by transfer of a fluorine atom to the benzene ring, perhaps as a result of the p → π interactions proposed by Sheppard. We propose that the mass spectra of the other benzene derivatives with highly fluorinated substituents investigated by Sheppard,[13] such as $SF_5 \cdot C_6H_5$ and $(CF_3)_2N \cdot C_6H_5$, will also show the monofluorobenzene ion and, by analogy to the present work, that the same groups attached to phosphorus will give PF_2^+ and PF^+ ions.

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Syntheses and Proton Magnetic Resonance Spectra of Some Arsonium and Phosphonium Compounds

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The reactions of a series of phenyl- and methyl-substituted arsines and phosphines with chloramine and with dimethylchloramine have been carried out, and the infrared and nmr spectra of the resulting aminophosphonium and aminoarsonium salts examined. The ^1H magnetic resonance data indicate $d\pi$–$p\pi$ bonding in both the arsonium and phosphonium compounds.

The reactions of tertiary phosphines with chloramine[1–4] and with dimethylchloramine[5] to give aminophosphonium chlorides have been investigated in detail in this laboratory. Tertiary arsines have been found to behave in an analogous way toward ammonia-free chloramine[6] and dimethylchloramine.[7] A study of the nuclear magnetic resonance spectra of the amino-

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TABLE I

ANALYTICAL DATA

Compound	Mp,[a] °C	% C		% H		% N		% Cl		% P or As	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[(CH_3)_3PN(CH_3)_2]Cl$	Not definite	38.59	38.32	9.72	9.90	9.00	9.14	22.78	23.05	19.90	19.70
$[(CH_3)_2P(C_6H_5)N(CH_3)_2]Cl$	131–132	55.18	53.37	7.87	8.24	6.43	6.66	16.29	16.85	14.23	13.25
$[(CH_3)P(C_6H_5)_2N(CH_3)_2]Cl$	134–135	64.40	63.06	6.85	7.23	5.01	5.24	12.67	12.80	11.07	11.20
$[(CH_3)_2As(C_6H_5)NH_2]Cl$	175 dec	41.14	39.42	5.61	6.20	6.00	5.86	15.18	15.20	32.07	31.72
$[(CH_3)As(C_6H_5)_2NH_2]Cl$	166–170 dec	52.81	50.91	5.11	5.88	4.74	4.40	11.99	11.57	25.34	23.99
$[(CH_3)_2As(C_6H_5)N(CH_3)_2]Cl$	132–134	45.90	43.69	6.55	6.80	5.35	5.43	13.55	13.34	28.64	28.90
$[(CH_3)As(C_6H_5)_2N(CH_3)_2]Cl$	131–132	55.66	53.73	5.92	6.23	4.33	4.36	10.95	10.33	23.15	24.35

[a] Some of these compounds soften at a considerably lower temperature than the melting or decomposition points, which are given in this table.

phosphonium salts[4] revealed several interesting relationships. It was of interest to us to know more about the reactions of dimethylchloramine with arsines and phosphines and to compare the proton magnetic resonance spectra of the phosphonium salts with those of the analogous arsonium salts in order to obtain information concerning the variation in the nature of the bonding in these two series of compounds.

Results reported herein indicate the formation of aminoarsonium and aminophosphonium salts, as expected. The proton magnetic resonance spectra of these compounds indicate $d\pi-p\pi$ bonding in the arsonium as well as in the phosphonium compounds. The synthetic procedures, analytical data, and infrared spectra of the new compounds prepared during this investigation are reported below.

Experimental Section

All operations were conducted in a moisture-free nitrogen atmosphere.

Materials.—Solvents used were dried over calcium hydride. Chloramine was produced by the gas-phase chlorination of ammonia as described earlier.[8] The ether solution of chloramine was freed from ammonia and dehydrated by the method of Gilson and Sisler.[9] Diphenylmethylarsine,[10] phenyldimethylarsine,[10] and dimethylchloramine[11] were prepared as reported in the literature. Trimethylarsine was made by the action of trimethylaluminum on arsenic trioxide[12] in toluene. Trimethylphosphine was synthesized by the action of CH_3MgI on phosphorus trichloride, distilled along with ether and the ethereal solution used as such for the reaction with dimethylchloramine.

Analysis.—Elemental analyses were carried out by the Galbraith Microanalytical Laboratories. Some of the arsenic, nitrogen, and chloride analyses were done in this laboratory. Analytical and melting point data are given in Table I.

Infrared and Proton Magnetic Resonance Spectra.—The infrared spectra were recorded with a Beckman Model IR-10 infrared spectrophotometer. The spectra of solids were taken in the form of Kel-F mulls for the range 2.5–7.5 μ and as Nujol mulls for the range 7.5–20 μ using KBr plates (Table II). Proton magnetic resonance spectra were recorded with a Varian A-60A spectrometer. The spectra of liquids were run as pure samples with tetramethylsilane (TMS) as internal standard and those of solids were determined in solution either in deuteriochloroform or in deuteriodimethyl sulfoxide (DMSO-d_6) with TMS or the sodium salt of 3-(trimethylsilyl)propanesulfonic acid (uvasol), respectively, as internal standard. The spectra of the liquid phosphines used in the present study were rerun[4] using TMS as internal standard. The concentration effect in DMSO using uvasol as internal standard was found to be within the experimental error (±0.02 τ unit) in the concentration range (3–12% by vol). A summary of the proton magnetic resonance data is given in Table III.

TABLE II

INFRARED DATA (cm^{-1})[a]

$[(CH_3)_3PN(CH_3)_2]Cl$

2960 s, 2900 w, 2820 w, 2450 w, 1460 w, 1430 w, 1315 vs, 1305 s, 1290 s, 1170 s, 1115 m, 1075 s, 990 vs, 970 vs, 960 vs, 895 sh, 885 s, 800 m, 770 s, 735 s, 720 sh, 625 w

$[(CH_3)_2P(C_6H_5)N(CH_3)_2]Cl$

3060 vw, 2994 sh, 2950 s, 2880 m, 2820 w, 2600 w, 2460 w, 1485 w, 1440 s, 1420 w, 1310 s, 1280 w, 1195 w, 1165 m, 1120 s, 1060 m, 1030 w, 1005 m, 990 sh, 970 s, 948 vs, 885 m, 760 vs, 745 s, 710 m, 700 w, 685 w, 640 w, 485 m

$[(CH_3)P(C_6H_5)_2N(CH_3)_2]Cl$

3060 vw, 2920 s, 2875 s, 2800 m, 1590 m, 1485 m, 1460 w, 1438 s, 1420 sh, 1325 m, 1315 m, 1280 w, 1175 s, 1115 vs, 1080 m, 1055 w, 1030 w, 1010 s, 980 s, 920 s, 900 m, 855 vw, 795 s, 750 vs, 718 vs, 690 vs, 650 vw, 510 s, 480 m, 460 s

$[(CH_3)_2As(C_6H_5)NH_2]Cl$

3130 w, 2950 s, 2920 s, 2850 sh, 2380 sh, 2250 m, 1480 w, 1370 w, 1255 w, 1150 w, 1105 m, 1085 s, 1020 w, 930 m, 897 s, 840 s, 775 m, 730 vs, 705 m, 685 m, 640 m, 610 m, 455 m

$[(CH_3)As(C_6H_5)_2NH_2]Cl$

3130–2720 b, s, 2400 sh, 1475 m, 1430 s, 1400 vs 1305 w, 1258 m, 1155 w, 1085 s, 1020 w, 965 w, 880 b, m, 800 m, 735 vs, 720 sh, 690 vs, 625 m, 460 b, m

$[(CH_3)_2As(C_6H_5)N(CH_3)_2]Cl$

3075 vw, 2975 s, 2900 m, 2805 m, 1490 vw, 1455 w, 1445 s, 1420 w, 1340 w, 1315 w, 1280 w, 1190 w, 1165 s, 1155 sh, 1110 w, 1090 s, 1050 s, 935 s, 910 vs, 865 m, 845 m, 740 vs, 720 sh, 685 s, 645 m, 615 s, d, 578 m, 462 s

$[(CH_3)As(C_6H_5)_2N(CH_3)_2]Cl$

3065 vw, 3020 sh, 2990 m, 2970 s, 2905 vw, 1485 w, 1450 s, 1445 sh, 1420 vw, 1150 s, 1090 s, 1045 m, 995 vw, 920 vs, 908 s, 760 sh, 755 vs, 720 w, 690 s, 635 w, 575 m, 460 s

[a] s, strong; m, medium; w, weak; sh, shoulder; d, doublet; b, broad.

Procedure for Chloramination Reactions.—The chloraminations of the arsines were carried out using anhydrous and ammonia-free chloramine solutions in ether on a vacuum line. In a typical reaction the ethereal solution of anhydrous, ammonia-free chloramine was taken into a flask connected to a vacuum line. The solution was transferred to a graduated tube at-

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TABLE III

PROTON MAGNETIC RESONANCE DATA

		X = P					X = As	
	Compound	τ_{CH_3}	τ_{NCH_3}	J_{PCH}, cps	J_{PNCH}, cps	Solvent	τ_{CH_3}	τ_{NCH_3}
1.	$(CH_3)_3X$[a]	9.11		2.7		Neat	9.10	
2.	$(CH_3)_2X(C_6H_5)$[b]	8.79		3.6		Neat	8.94	
3.	$(CH_3)X(C_6H_5)_2$	8.58		4.4		Neat	8.72	
4.	$[(CH_3)_3XNH]_2Cl$[c]	8.09		14.5		DMSO-d_6	8.21	
5.	$[(CH_3)_2X(C_6H_5)NH_2]Cl$[c]	7.81		14.5		DMSO-d_6	7.95	
6.	$[(CH_3)X(C_6H_5)_2NH_2]Cl$[c]	7.39		14.1		DMSO-d_6	7.65	
7.	$[(CH_3)_3XN(CH_3)_2]Cl$[d]	7.94	7.30	14.0	11.5	DMSO-d_6	8.28	7.52
		7.67	7.14	14.0	11.5	$CDCl_3$	7.50	7.22
8.	$[(CH_3)_2X(C_6H_5)N(CH_3)_2]Cl$	7.29	7.11	13.5	11.5	$CDCl_3$	7.15	↔ 7.17
9.	$[(CH_3)X(C_6H_5)_2N(CH_3)_2]Cl$	6.92	7.07	13.5	11.0	$CDCl_3$	6.76	7.10
10.	$[(CH_3)_4X]I$[e]	8.08		14.8		DMSO-d_6	8.00	
11.	$(CH_3)_2NCl$		7.15			Neat		

[a] For nmr data of $(CH_3)_3P$, see ref 13. [b] Nmr data of $(CH_3)_2P(C_6H_5)$ have been reported in benzene, τ 8.89, $J_{\mathrm{PCH}} = 3.7$ cps, and in $CDCl_3$, τ 8.61, $J_{\mathrm{PCH}} = 1.7$ cps, by J. M. Jenkins and B. L. Shaw, *J. Chem. Soc., Sect. A*, 770 (1966). [c] Other data on compounds when X = P have been reported in ref 4. [d] Analytical data of $[(CH_3)_3AsN(CH_3)_2]Cl$ to be published. [e] Nmr data of $(CH_3)_4PI$ in $CDCl_3$, τ 7.53, $J_{\mathrm{PCH}} = 14.4$ cps, reported by ref 13, could not be repeated in this laboratory owing to insolubility of this compound in $CDCl_3$.

tached to the vacuum line and degassed; a 1-ml sample was taken out by means of a syringe to find out the exact concentration of the chloramine solution. The volume of the remaining solution was noted and was shown to contain (0.44 g, 0.00854 mol) of chloramine. The solution was again degassed and transferred completely onto a degassed solution of diphenylmethylarsine (2.08 g, 0.00852 mol) in 10 ml of dry ether kept at liquid nitrogen temperature. Apparently no reaction occurred at this temperature. As the temperature was raised to room temperature a white solid started to form in the reaction flask. The mixture was stirred for 2 hr and after that all of the ether was distilled out leaving behind 2.4 g of a white solid, which was again washed with ether and dried under vacuum. The yield was 95.3% based on the arsine.

The reactions of dimethylchloramine with tertiary arsines and phosphines were carried out at room temperature and atmospheric pressure. In a typical reaction, diphenylmethylarsine (1.92 g, 0.0079 mol) was dissolved in 20 ml of ether and allowed to react with an excess of dimethylchloramine (mole ratio 1:5). After a little while a white cloudy precipitate began to form. The reaction mixture was stirred overnight, filtered in the drybox, washed with ether, and dried under vacuum. The yield was 1.85 g, 72.7% based on the arsine.

The reactions of dimethylchloramine with tertiary arsines, in general, are much slower than those with tertiary phosphines. The arsonium salts are difficult to crystallize and often are obtained in a lower degree of purity when recrystallized from chloroform. The dimethylaminophosphonium salts, being extremely soluble in chloroform, can be precipitated out by carefully adding the chloroform solution to an excess of ether. The arsonium salts, like the phosphonium derivatives, are extremely sensitive to moisture.

Results and Discussion

The chemical shifts and coupling constants of the methyl protons are presented in Table III. In general, the proton magnetic resonance spectra of arsonium compounds are similar to those of phosphonium salts, except for the fact that the proton resonances of the phosphonium compounds have the expected multiplicity resulting from the spin–spin coupling with ^{31}P. The strongest peak of phenyl proton resonances in the neutral phosphines and arsines occur in the range τ 2.7–2.9, whereas in the case of phosphonium or arsonium salts they lie in the range τ 2.2–2.3. The dimethylamino proton resonances are almost unaffected by substitution either on phosphorus or arsenic in $CDCl_3$. No resonance signal was observed for NH_2 protons in diphenylmethylaminoarsonium chloride or dimethylphenylaminoarsonium chloride. Presumably, this signal lies underneath the phenyl proton signal as indicated by the area ratio of the phenyl and methyl proton resonances in these compounds. In the case of trimethylaminoarsonium chloride, the NH_2 signal appears as a very broad signal, $\tau \sim 2.5$. It is interesting to note here that the line width of NH_2 signal increases in the order, hydrazinium < phosphonium < arsonium salts. It may be that the line widths in these cases are governed by the quadrupole interactions of the nitrogen nucleus. In the hydrazinium salts the electric field gradient may be less around the nitrogen nucleus as compared with the phosphonium and arsonium salts, since the symmetry is greater in the first case.

In the absence of data concerning NH_2 signals in the spectra of the arsonium salts, it is worthwhile to discuss the results in terms of the chemical shifts of methyl proton resonances. As expected, signals corresponding to the methyl protons attached to phosphorus or arsenic atoms are shifted downfield when the phosphorus or arsenic atoms are quaternized. This is presumably a result of the presence of a positive charge on the arsenic or phosphorus atoms.[4,13] The methyl proton resonance in the aminophosphonium chlorides undergoes an almost linear downfield shift when methyl groups are successively replaced by phenyl groups. The same phenomenon is also observed in the case of tributylmethylphosphonium iodides,[14] when a butyl group is replaced by a phenyl group. This might be explained in terms of the phenyl group being more electronegative than the methyl or butyl group; this would cause a reduction in the electron density on the methyl protons as a result of the changed inductive effect. However, the chemical shift of the methyl protons of the tetramethylphosphonium iodide (τ 8.08) is almost equal to that of trimethylaminophosphonium chloride (τ

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8.09), though the amino group is more electronegative than the methyl or phenyl group. The chemical shifts of phosphonium salts are not affected by halide ion,[14] and it is reasonable to assume dπ–pπ bonding between the phosphorus and nitrogen atom of the amino group. Because of this π bonding the phosphorus would become less positive and consequently methyl protons would be more shielded, resulting in the observed chemical shift of the trimethylaminophosphonium chloride. Thus the effect of the π bonding largely nullifies the effect of the electronegativity of the amino group. Considerable amounts of π bonding have been reported in quadruply connected phosphorus compounds containing nitrogen.[15] Dimethylaminophosphonium compounds show similar trends in chemical shifts in chloroform solution as a result of substitution of phenyl groups. A comparison of the chemical shift of methyl protons of trimethyldimethylaminophosphonium chloride and trimethylaminophosphonium chloride in DMSO indicate almost equal amounts of π bonding in these compounds.

The effect of phenyl group substitution on the chemical shift of methyl protons in amino and dimethylaminoarsonium compounds is similar to that in the case of phosphonium compounds as seen from Table III. Assuming again that anions do not affect the chemical shift, a comparison of the methyl proton resonances of tetramethylarsonium iodide (τ 8.00) with that of amino- (τ 8.21) or dimethylaminotrimethylarsonium chloride (τ 8.28) in DMSO indicates dπ–pπ bonding between arsenic and nitrogen atoms in these compounds. It is difficult to draw any conclusion from the comparison of the methyl proton chemical shifts of the arsonium and phosphonium chlorides, in general, with regard to the extent of dπ–pπ bonding. However, these data seem to indicate more π bonding in the arsonium compounds than in phosphonium compounds.

The magnitudes of the coupling constants, J_{PCH}, increase when the phosphorus atom is quaternized and both J_{PCH} (14.0 ± 0.4 cps) and J_{PNCH} (11.3 ± 0.3 cps) remain constant regardless of the other substituents on the phosphorus atom in these methyl-substituted phosphonium compounds as observed earlier.[4,14]

The infrared spectra of amino and dimethylaminophosphonium chlorides have been reported earlier.[2–5] In cases where one or more phenyl groups were attached to phosphorus, these quaternary phosphonium salts display a strong and sharp characteristic band at 1120 ± 10 cm^{-1}. A careful examination of the infrared spectra of quaternary arsonium salts in the present study show a sharp band of strong intensity at 1085–1090 cm^{-1}. This band again appears in all compounds where one or more phenyl groups are attached to quaternary arsenic, but is absent in trimethylaminoarsonium chloride.[6] Another infrared spectral study of tetraphenylarsonium salts with 12 different anions by Al-Kayssi and Magee[16] also show this band, though unassigned, appearing almost unchanged in every case. It seems to us that this band may be taken as a characteristic band for quaternary arsonium salts where one or more phenyl groups are attached to the arsenic atom. Other major peaks in the infrared spectra of the arsonium salts which can be readily recognized in the present case are: CH stretch in 3000-cm^{-1} region, CH in-plane vibration at 1445–1490 cm^{-1}, and the C=C out of plane vibration at 750 cm^{-1}. The NH stretching frequency generally occurs in the 3100-cm^{-1} region in the aminoarsonium chlorides. The AsC stretch, which has been assigned as a strong, broad band occurring at 474 cm^{-1} in triphenylarsine,[17] probably occurs in the range 460 cm^{-1} in the arsonium salts as observed in this investigation.

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