The results also agree with those of Sisler and coworkers.[3]

Formulation of the initial reaction product as I is supported by its rapid reaction with water to give the appropriate phosphine oxide. It was also shown that the initial precipitate reacts with various alcohols to give alkyl halides and olefins. Phenol reacted to give tris(dialkylamino)phenoxyphosphonium chlorides.[10] These results clearly show that the first product is not a tris(dialkylamino)chlorophosphonium chloride. Nöth and Vetter[6] have shown that tris(dimethylamino)chlorophosphonium chloride is stable in aqueous media. Their findings have been confirmed.[10]

It is clear though that I does undergo further reaction to give tris(dialkylamino)chlorophosphonium chloride. A possible path for the generation of this salt involves reaction of the dialkylamide ion with N-chlorodialkylamine to generate chloride ion, Schiff base (II), and tris(dialkylamino)chlorophosphonium chloride (III). There is precedence for such an elimination reaction.[11] That a Schiff base is formed as a product of the reaction with N-chlorodibenzylamine has been demonstrated and its formation can certainly be inferred by the isolation of the 2,4-dinitrophenylhydrazone of acetaldehyde from the N-chlorodiethylamine reaction. This reaction scheme is supported by the observed stoichiometry which is 1 mol of phosphine to 2 mol of N-chlorodialkylamine. It is also supported by the finding that tris(diethylamino)chlorophosphonium chloride reacted with lithium diethylamide to give tris(diethylamino)phosphine. This demonstrates that the formation of I is reversible and thus a route is available for the formation of the observed products.

$$\mathrm{I} + (\mathrm{RCH_2})_2\mathrm{NCl} \longrightarrow \underset{\mathrm{III}}{(\mathrm{R_2N})_3\overset{+}{\mathrm{P}}\mathrm{Cl}} + \mathrm{Cl^-} + \underset{\mathrm{II}}{\mathrm{RCH{=}NCH_2R}} + (\mathrm{RCH_2})_2\mathrm{NH}$$

It is important to note that this appears to be the first example of direct proof that the phosphine is attacking the halogen of the N–X compound with the production of a halophosphonium salt. Unfortunately these results cannot be generalized to other phosphorus-containing nucleophiles.

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[10] The details of these experiments can be found in the Ph.D. thesis of S. M. Felton, Rutgers, The State University, 1967.

[11] (a) W. E. Bachmann, M. P. Cava, and A. S. Dreiding, *J. Am. Chem. Soc.*, **76**, 5554 (1954); (b) H. E. Baumgarten and F. A. Bower, *ibid.*, **76**, 4561 (1954); (c) F. Klages, *Ann.*, **547**, 1 (1941).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

Fragmentation and Rearrangement Processes in the Mass Spectra of Fluoroalkylphosphorus Compounds. I. Trifluoromethylphosphines and Trifluoromethylhalogenophosphines

BY R. G. CAVELL AND R. C. DOBBIE

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The mass spectra of a series of trifluoromethylhalogeno- and hydridophosphines have been studied. In addition to normal bond breaking, extensive rearrangement of the ions was observed leading to species containing P–F bonds in all of the spectra. A mechanism for the transfer of fluorine from carbon to phosphorus is proposed.

Introduction

The mass spectra of pentafluorophenylphosphorus derivatives indicated that both normal fragmentation and molecular rearrangement occurred under electron impact.[1] Also it has been recently demonstrated that the trifluoromethyl derivatives of arsenic undergo extensive rearrangement under electron impact to form ions and neutral fragments containing As–F bonds.[2] We have made a comprehensive study of the mass spectra of trifluoromethylphosphorus compounds to evaluate the importance of rearrangement processes.

Experimental Section

Standard vacuum techniques were used for all manipulations. The compounds were prepared from the iodophosphines[3] by the most convenient literature methods. The action of antimony trifluoride,[4,5] mercuric chloride, and mercuric bromide[5,6] gave the corresponding fluoro, chloro, and bromo compounds, while reduction with hydrogen iodide and mercury gave the hydrides.[7] Pure samples of the iodophosphines for mass spectroscopic study were obtained from the reaction of iodine with either tetrakis(trifluoromethyl)diphosphine[3] or with a mixture of trifluoromethylphosphorus cyclic tetramer and pentamer.[8] The compounds were characterized and purified as described in the literature.[3–8] In general, gas-phase molecular weights within 0.5% of the theoretical value were obtained on all compounds. The infrared spectra agreed with the literature and showed no indication of impurities. Comparison of the results of vapor pressure measurements on some of the compounds with the

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[1] J. M. Miller, *J. Chem. Soc., Sect. A*, 828 (1967).

[2] R. C. Dobbie and R. G. Cavell, *Inorg. Chem.*, **6**, 1450 (1967).

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[4] A. B. Burg and G. Brendel, *J. Am. Chem. Soc.*, **80**, 3198 (1958).

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[6] A. B. Burg and J. F. Nixon, *J. Am. Chem. Soc.*, **86**, 356 (1964).

[7] R. G. Cavell and R. C. Dobbie, *J. Chem. Soc., Sect. A*, 1308 (1967).

[8] W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, **80**, 6161 (1958).

literature[3-8] also confirmed their purity. Finally the absence of peaks which could be assigned to the starting materials in the mass spectra of the compounds studied provided a further criterion of their purity.

Mass spectra were determined with an AEI MS-9 spectrometer with the heated inlet system at 185°; the ionization voltage was 70 ev. Some of the spectra were also recorded using a room-temperature inlet system with only minor variations in intensity of the major peaks being observed. Perfluorotri-*n*-butylamine was used as a standard for mass measurement.

Results and Discussion

The mass spectra of the phosphorus compounds are unfortunately more difficult to analyze than those of arsenic, because of the small difference in the masses of P and CF (0.0246 amu). However, interpretation of the spectra was made possible by mass measurement of ambiguous peaks at high resolution, although in some cases nearly all of the ions in the spectrum had to be examined in this way. The compounds studied were the trifluoromethyl derivatives, CF_3PX_2, the bis(trifluoromethyl)phosphines, $(CF_3)_2PX$, where X = H, F, Cl, Br, and I, and tris(trifluoromethyl)phosphine, $(CF_3)_3P$. Rearranged ions were present in all of the spectra.

The observed spectra, including the results of high-resolution studies, are shown in Tables I and II while Table III lists some of the metastable ions along with their assignment. It is apparent from the tabulated results that there are two simultaneous breakdown pathways, one of normal fragmentation and another which involves rearrangement of the fluorine atoms from carbon to phosphorus. In the compounds containing only one trifluoromethyl group, it is evident from the intensity of the ions in the spectrum that the major fragmentation of the parent ion occurred at the C–P bond, giving CF_3 and PX_2 fragments, either of which may be charged. Likewise normal fragmentation of the bis(trifluoromethyl)phosphines proceeded through the elimination of a CF_3 group rather than the elimination of a halogen or hydrogen atom except in the case of iodobis(trifluoromethyl)phosphine which exhibited primary fragmentation at the P–I bond to yield an intense ion at *m/e* 169 ($C_2F_6P^+$, 3.5%) and I^+ (3.7%). The loss of the iodine atom from the parent ion was also demonstrated by the metastable peak at *m/e* 96.6. In addition to loss of CF_3 in the normal fragmentation process, the bis(trifluoromethyl)phosphines were also observed to eliminate CF_4 from the molecular ion to yield CF_2PX ions, a process which was demonstrated by the observation of the appropriate metastable ion in the mass spectrum of more than one of the compounds. Judging from the relative intensities of the CF_2PX and CF_3PX ions, the elimination of CF_4 from the molecular ion rather than CF_3 appears to be the preferred decomposition pathway.

Table I

Mass Spectra of Trifluoromethylphosphino Compounds CF_3PX_2

Ion	Intensity^{a,b}				
	X = I^c	X = Br^{d,e}	X = Cl^d	X = F	X = H^f
CF_3PX_2	34.4	15.4	15.2	4.6	27.3
CF_3PX				3.5	0.5
CF_2PX_2			1.7		3.1
PX_2	22.6	49.8	55.4	29.8	2.2
PX	8.3	6.9	5.8	2.0	3.2
P	1.4	1.0	0.8		1.5
CF_3	3.8	6.8	4.4	51.0	27.3
CF_2		0.7		2.5	0.6
CF	1.6	1.0	0.9	5.7	2.1
PF_2^{b}	2.9	2.6	3.5		13.5
PFX^b	11.2	12.4	11.2		2.3
PF^b	2.0	1.2	1.0		3.0

[a] Intensities are expressed as per cent total ionization, defined as $\Sigma(\text{Int})_n$ where n refers to all ions with $m/e > 30$ whose intensity is >2% of the base peak. [b] Ions are listed only once in the table under the most general designation. [c] Also observed: I^+ (11.8%). [d] Summed over isotopes. [e] Also observed: Br^+ (2.3%). [f] Also observed: CF_2PH^+ (1.2%), CF_2P^+ (1.4%), $CFPH^+$ (1.0%), CFP^+ (0.8%), PFH_2^+ (3.5%), CF_2H^+ (4.6%), CFH_2^+ (1.1%).

Table II

Mass Spectra of Bis(trifluoromethyl)phosphino Compounds, $(CF_3)_2PX$, and Tris(trifluoromethyl)phosphine

Ion	Intensity^{a,b}					
	X = I^c	X = Br^d	X = Cl^d	X = F^e	X = H^f	X = CF_3
C_2F_6PX	38.0	15.5	13.0	8.0	10.1	2.5
C_2F_5PX				1.3	4.4	4.7
CF_3PX	7.7	3.4	1.4	5.1	4.1	
CF_2PX	2.8	11.3	8.5		9.6	3.0
CFPX				1.5	1.8	8.6
PX	3.5	2.8	2.8	3.5	0.9	4.6
P		0.8	1.0		0.8	
CF_3P	1.9	2.0	1.2		1.7	
CF_2P	1.1	1.3	1.1		1.7	1.9
CFP		0.7			0.9	1.4
CF_3	11.9	29.8	30.5	29.2	39.4	52.5
CF_2		0.8	0.7	1.3		2.4
CF	2.0	2.7	2.4	9.1	3.1	4.1
CF_4P	1.0		0.8			
PF_2	8.2	6.3	9.7	33.0	12.5	13.0
PFX^b	13.6	20.6	25.3		3.1	
PF^b	1.5	1.6	1.6		1.9	1.5

[a] Intensities are expressed as per cent total ionization, defined as $\Sigma(\text{Int})_n$ where n refers to all ions with $m/e > 30$ whose intensity is >2% of the base peak. [b] Ions are listed only once in the table under the most general designation. [c] Also observed: $C_2F_6P^+$ (3.5%), I^+ (3.7%). [d] Summed over isotopes. [e] Also observed: $C_2F_4^+$ (8.1%). [f] Also observed: CF_2H^+ (4.1%).

The mass spectra of all of the trifluoromethylphosphines, including tris(trifluoromethyl)phosphine, showed fairly intense peaks corresponding to the ions PF_2^+, PFX^+, and PF^+. Although PF_2^+ and PF^+ could result from normal fragmentation of CF_3PF_2 and PF^+ from normal fragmentation of $(CF_3)_2PF$, all of the other trifluoromethyl derivatives must have undergone rearrangement under electron impact. Rearranged fluorocarbon species (CF_2Cl^+ and $CFCl^+$) were observed as ions of low intensity in CF_3PCl_2 but not observed in the dibromo or diiodo derivatives. In all of the dihalogeno compounds, very weak ions (<0.5% of the base peak) corresponding to PFX_2^+ were found. In contrast, the hydride, CF_3PH_2, gave relatively intense peaks corresponding to PFH_2^+ (*m/e* 52, 3.5%) as well as to CF_2H^+ (*m/e* 51, 4.6%) and CFH_2^+ (*m/e* 33, 1.1%). The first of these ions is thought to be formed from the molecular ion

$$CF_3PH_2^+ \longrightarrow PFH_2^+ + CF_2 \qquad (1)$$

TABLE III

METASTABLE IONS IN THE MASS SPECTRA OF TRIFLUOROMETHYLPHOSPHINES

Compound	*m/e*		Transition
	Obsd	Calcd	
CF_3PH_2	47.8	47.8	$CF_2PH_2^+ \rightarrow CFPH^+ + HF$
	47.0	46.9	$CF_2PH^+ \rightarrow CFP^+ + HF$
	46.7	46.7	$CF_3PH_2^+ \rightarrow 69^+ + 33$
	25.5	25.5	$CF_3PH_2^+ \rightarrow 51^+ + 51$
$(CF_3)_2PI$	96.6	96.5	$C_2F_6PI^+ \rightarrow C_2F_6P^+ + I$
	28.2	28.2	$C_2F_6P^+ \rightarrow 69^+ + 100$
$(CF_3)_2PBr$	105.0, 103.0	105.0, 103.2	$C_2F_6P^{81,79}Br^+ \rightarrow CF_2P^{81,79}Br^+ + CF_4$
	74.3, 72.7	74.3, 72.7	$C_2F_5P^{81,79}Br^+ \rightarrow PF^{81,79}Br^+ + C_2F_4$
$(CF_3)_2PCl$	67.5, 65.8	67.6, 66.0	$C_2F_6{}^{37,35}Cl^+ \rightarrow CF_2P^{37,35}Cl^+ + CF_4$
	40.5, 39.1	40.5, 39.1	$C_2F_5P^{37,35}Cl^+ \rightarrow PF^{37,35}Cl^+ + C_2F_4$
$(CF_3)_2PF$	75.3	75.3	$C_2F_7P^+ \rightarrow CF_4P^+ + CF_3$
	53.2	53.2	$C_2F_7P^+ \rightarrow C_2F_4^+ + PF_3$
	28.3	28.2	$C_2F_6P^+ \rightarrow 69^+ + 100$
$(CF_3)_2PH$	60.0	60.0	$C_2F_6PH^+ \rightarrow CF_3PH^+ + CF_3$
	39.5	39.6	$C_2F_6PH^+ \rightarrow CF_2PH^+ + CF_4$
	31.5	31.5	$C_2F_5PH^+ \rightarrow 69^+ + 82$
	17.2	17.2	$C_2F_5PH^+ \rightarrow 51^+ + 100$
$(CF_3)_3P$	94.6	94.5	$C_3F_9P^+ \rightarrow C_2F_5P^+ + CF_4$
	78.5	78.4	$C_3F_8P^+ \rightarrow C_2F_4P^+ + CF_4$
	36.4	36.3	$C_2F_4P^+ \rightarrow 69^+ + 62$
	31.8	31.7	$C_2F_5P^+ \rightarrow 69^+ + 81$
	25.6	25.6	$C_2F_5P^+ \rightarrow 62^+ + 88$

although the corresponding metastable peak was not observed. Most of the compounds studied here have been shown to eliminate CF_2 in flash photolysis experiments,[9] apparently by an intramolecular process. Further, the trifluoromethylfluorophosphoranes have been reported to decompose thermally by elimination of CF_2.[10] Thus it is reasonable to propose that decomposition by elimination of CF_2 from the trifluoromethyl group under electron impact may yield ions containing P–F bonds. Few metastable ions were detected in the spectra, and for this reason the route of formation of the rearranged ions must remain in doubt. However, the metastable ion at *m/e* 25.5 in the spectrum of CF_3PH_2 did indicate a rearrangement, although it was not possible to say whether (2) or (3) or both (2) and (3) took place as the ion at *m/e* 51 was a

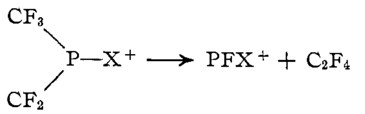
$$CF_3PH_2^+ \longrightarrow CF_2H^+ + PFH \qquad (2)$$

$$CF_3PH_2^+ \longrightarrow PFH^+ + CF_2H \qquad (3)$$

doublet. It seems plausible that the rearranged ions in all of the compounds CF_3PX_2 also arise from the parent, by the process

$$CF_3PX_2^+ \longrightarrow PFX^+ + CF_2X \qquad (4)$$

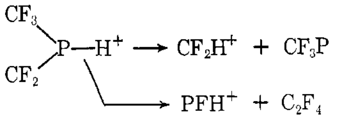
It is also noteworthy that the peak at *m/e* 100 in $(CF_3)_2PF$ was a doublet consisting mainly of $C_2F_4^+$, formed from the molecular ion by elimination of a molecule of PF_3, with a very small amount only of CF_3P^+. In all of the other compounds of the bis(trifluoromethyl) series, this ion was largely CF_3P^+ with a trace of $C_2F_4^+$. This is in interesting contrast to the results found by Miller[1] for pentafluorophenylphosphorus derivatives where $(C_6F_4)_2^+$ was found to be an intense ion in the mass spectrum of compounds containing the $(C_6F_5)_2P$ group. Although the $(M-F)^+$ ion (where M is the molecular ion) had a low intensity in some of the spectra, it seemed to be the source of the PFX^+ ion, since metastable ions were observed in the chloro and bromo compounds corresponding to the transition


(5)

The metastable peak at *m/e* 28.3 in the mass spectrum of $(CF_3)_2PF$ could be attributed to elimination of either C_2F_4 or CF_3P from $C_2F_6P^+$. By analogy to the chloro and bromo compounds, the former assignment is preferred, *i.e.*

$$C_2F_6P^+ \longrightarrow PF_2^+ + C_2F_4 \qquad (6)$$

The interpretation of the metastable peak at *m/e* 17.2 in the spectrum of the hydride is likewise ambiguous; it can be assigned to either of the processes


(7)

(8)

since the ion at *m/e* 51 was a doublet. Comparison with the halogenophosphines would suggest that eq 8 holds. However, an investigation of the mass spectrum of the arsine,[2] $(CF_3)_2AsH$, has shown that an equation analogous to (7) can describe the formation of CF_2H^+ in that compound. It seems probable that both (7) and (8) occur in the phosphine.

The mass spectrum of tris(trifluoromethyl)phosphine was similar to that of the $(CF_3)_2P$ compounds, showing a moderately intense rearrangement ion at *m/e* 69 (PF_2^+, 13.0%). The molecular ion could lose a fluorine atom or CF_4 as the primary process. In the former

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[9] R. G. Cavell, R. C. Dobbie, and W. J. R. Tyerman, *Can. J. Chem.*, **45**, 2849 (1967).

[10] W. Mahler, *Inorg. Chem.*, **2**, 230 (1963).

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

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

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

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

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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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA 32601

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

BY HARRY H. SISLER AND SAMPAT R. JAIN

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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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