Aryl-substituted Fluorophosphazenes. Part VII.[1] Mass Spectra of some Aryl-substituted Fluorocyclotriphosphazenes

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The mass spectral data for a series of aryl substituted fluorocyclotriphosphazenes, $P_3N_3F_nAr_{6-n}$ (n = 2, 4, or 5; Ar = C_6H_5, C_6D_5, or p-$C_6H_4NMe_2$), are reported and discussed. Successive loss of aryl groups, leaving the phosphazene ring intact is the major fragmentation process for the geminal derivatives while linear ion formation is the most significant process for the non-geminal isomers. Intensity differences are noted between the spectra of the *cis* and *trans* 1,3-$P_3N_3F_4(C_6H_5)_2$ species. The nature of the aryl group has a pronounced effect on the fragmentation processes. A variety of fragmentation and rearrangement processes are discussed in relation to the known structural properties and solution chemistry of the cyclotriphosphazenes.

As opposed to n.m.r. and vibrational spectroscopy, mass spectroscopy has not been applied extensively to the characterization of phosphazene derivatives.[2] The mass spectra of the fluorocyclophosphazenes, $(PNF_2)_{3-16}$,[3] chlorocyclophosphazenes, $(PNCl_2)_{3-8}$,[4] chlorobromocyclotriphosphazenes, $P_3N_3Cl_nBr_{6-n}$,[5] bromocyclophosphazenes, $(PNBr_2)_{3-6}$,[6] and isothiocyanatocyclophosphazenes, $[PN(NCS)_2]_{3,4}$,[7] have been studied in detail. The fragmentation patterns observed in these studies are fairly complex, giving rise to rearranged and multiply charged ions in addition to a large variety of cyclic and linear species. The halogen substituted phosphazenes produce linear ions of the type $P_nN_{n-1}X_y^+$ in addition to cyclic ions, while the isothiocyanatocyclophosphazenes experience extensive fragmentation at the exocyclic positions resulting in a variety of cyclic ions. Since several of the basic fragmentation routes of the cyclophosphazenes have been elucidated, we felt that it would be of interest to investigate the mass spectra of a series of substituted phosphazenes of known structure in order to see if any correlations between structure and fragmentation pattern could be made. We chose to study the series $P_3N_3F_nAr_{6-n}$ [n = 2, 4, or 5; Ar = C_6H_5, C_6D_5, or p-$C_6H_4N(CH_3)_2$] because both geminal[8,9] and non-geminal[9,10] isomers are known and substantial differences in the bond energies of the two types of substituents (F and Ar) probably occur. Information of this type will hopefully lead to further development of mass spectroscopy as a tool for structural characterization of phosphazene derivatives.

EXPERIMENTAL

Materials.—Phenyl substituted fluorocyclotriphosphazenes were prepared by previously reported procedures.[8,10,11] Deuteriated phenylfluorocyclotriphosphazenes were prepared by analogous procedures employing perdeuteriophenyl-lithium (C_6D_5Li) in place of phenyl-lithium. The synthesis and characterization of the p-*NN*-dimethylaminophenyl derivatives will be discussed in a subsequent publication.[9]

Measurements.—The mass spectra were obtained on a Perkin-Elmer RMU-6D mass spectrometer operating at 80 eV and 125°. Samples were admitted through the hot inlet system. Perfluorokerosene was employed as a calibrant.[12]

RESULTS AND DISCUSSION

As expected, the mass spectra of the arylfluorocyclotriphosphazenes are rich in fragmentation products of both the aryl and phosphazene ring systems. The mass spectral data for the arylpentafluorocyclotriphosphazenes may be found in Table 1. The assignments

TABLE 1

Selected mass spectra of molecules of the type $P_3N_3F_5Ar$ [Ar = C_6H_5, $C_6H_4N(CH_3)_2$]

m/e		Relative abundance		
C_6H_5	$C_6H_4N(CH_3)_2$	C_6H_5	$C_6H_4N(CH_3)_2$	Assignment
307	350	100	100	$P_3N_3F_5Ar^+$
288	331	3·0	2·7	$P_3N_3F_4Ar^+$
287	330	3·0	0·2	$P_3N_3F_4(Ar - H)^+$
242	242	10·3	1·5	$P_3N_3F_5C^+$
231	231	3·0	1·7	$P_3N_3F_5H^+$
230	230	14·2	12·7	$P_3N_3F_5^+$
216	216	40·9	10·9	$P_3N_2F_5^+$
212	212	2·4	1·2	$P_3N_3F_4H^+$
211	211	2·4	0·8	$P_3N_3F_4^+$
197	197	9·7	5·0	$P_3N_2F_4^+$
171	171	11·5	4·7	$P_2NF_5^+$
153·5	175	1·4	9·8	$P_3N_3F_5Ar^{2+}$
152	152	7·3	3·1	$P_2NF_4^+$
133	133	3·0	1·7	$P_2NF_3^+$
114	114	9·4	4·2	$P_2NF_2^+$
107	107	4·8	1·7	$PN_2F_2^+$
91		7·9		$C_6H_5N^+$
77		13·3		$C_6H_5^+$
69		16·6		$PF_2 + P_2N^+$
65		3·0		$C_5H_5^+$
51		25·5		$C_4H_3^+$
39		38·2		$C_3H_3^+$

for the hydrocarbon containing fragments of the monophenyl derivatives have been verified by comparison to the mass spectrum of $P_3N_3F_5C_6D_5$. The lower region

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of the spectra (m/e <100) is dominated by the fragmentation of the aryl group and the representative ions reported in Table 1 are those which are usually found in the spectra of aryl derivatives [13] and appear in all the spectra reported in this paper.

The peak at m/e 91 in the spectrum of $P_3N_3F_5C_6H_5$ can be assigned to the $C_6H_5N^+$ ion which results from a phenyl migration from a phosphorus to a nitrogen atom followed by elimination of the C_6H_5N fragment. Migration of substituents with substantial positive character from phosphorus to nitrogen sites has been observed in phosphazene chemistry.[14] In the ionization of $P_3N_3F_5C_6H_5$, the electron would be lost from the phenyl group since the ionization potential for nitrobenzene [15] is lower than those of the fluorocyclotriphosphazenes [16] and the $P_3N_3F_5$ group has been shown to be equivalent to the nitro-group in electron withdrawing power.[1] The electron deficiency of the ionized phenyl group would favour interaction with the electron rich nitrogen centre. The resulting ion, $P_3N_2F_5^+$, is second only to the parent ion in intensity which also suggests a facile loss of C_6H_5N. The related $P_3N_2F_4^+$ ion is also of appreciable intensity. By comparison, the $P_3N_2F_5^+$ ion is of fairly low intensity in the mass spectrum of $P_3N_3F_6$.[3] The mass spectrum of $P_3N_3F_5[C_6H_4N(CH_3)_2]$ exhibits a much lower intensity for the $P_3N_2F_5^+$ ion and does not contain the $(CH_3)_2NC_6H_4N^+$ ion. Apparently the strongly electron donating *NN*-dimethylamino-group reduces the electron deficiency of the aryl group in the parent ion so the migration process is no longer favourable. This increased electron rich character is also reflected in the much larger abundance of the doubly charged parent ions in the *NN*-dimethylanilino- compared to phenyl derivatives. The intensities of the P_2NF_n and PN_2F_n linear ions are comparable to the same series of ions in the spectrum of $P_3N_3F_6$.[3] The observed linear ions are all fluoride derivatives rather than phenyl containing species. This observation supports the conclusion of Wagner and Moeller that the linear ions are best stabilized by halogen substituents.[7]

The intensity of the $P_3N_3F_5^+$ ion is substantially greater than the $P_3N_3F_4Ar^+$ ion reflecting the more facile cleavage of the phosphorus–carbon compared to the phosphorus–fluorine bond. The $P_3N_3F_5^+$ peak has a strong $P + 1$ peak which is a $P + 2$ peak in the spectrum of the deuteriated derivative. This peak thus represents the $P_3N_3F_5H^+$ fragment. Protonated fragments have been detected in the mass spectra of other phosphazene derivatives.[17]

The formation of the $P_3N_3F_5C^+$ ion results from loss of C_5H_5 from the parent ion. This type of behaviour is well established for monosubstituted benzene derivatives.[13]

The spectra of all the *p-NN*-dimethylanilino-derivatives show intense peaks resulting from fragmentation of the *NN*-dimethylamino-group in the parent ion.

The spectra of the various disubstituted compounds exhibit the general features indicated for the monosubstituted species. The high mass fragments of interest in the spectra of the disubstituted fluorocyclotriphosphazenes are summarized in Table 2. In addition to the ions in Table 2 and some unidentified species, the spectra exhibit the aryl group fragmentation products and an array of fluorine containing linear phosphorus–nitrogen ions similar to those observed for the monosubstituted fluorocyclotriphosphazenes.

Substantial differences in the mass spectra of the diphenyl geminal and non-geminal isomers are observed. The most important process in the fragmentation of the geminal isomer is successive loss of phenyl groups leaving the ring intact. The intensity of the $P_3N_2F_4^+$ ion in the geminal isomer is fairly low indicating low tendency to form the linear ion.

In the spectra of the non-geminal isomers the successive loss of phenyl groups is replaced by linear ion formation as the major fragmentation pathway. Linear ion formation appears to be related to the availability of at least one fluorine atom on each phosphorus atom. The most dramatic difference in the ability to form linear ions is the seven-fold increase in the intensity of the $P_3N_2F_4^+$ ion on going from the geminal to the non-geminal isomers. Loss of a nitrogen or a fluorine atom from the parent ion is observed. However, the loss of NH and HF appear to be more favourable. The loss of each of these diatomic molecules from the parent ion is confirmed by observation of the metastable ions corresponding to these processes (Table 3). The loss of the fluorine atom from the non-geminal isomers occurs more readily than in the geminal isomer. The fact that HF formation is observed in the non-geminal isomer may be related to the geminal disposition of the phenyl group and the fluorine atom thus placing the fluorine and hydrogen atoms in close enough proximity to allow formation of HF.

Both the *cis* and *trans* 1,3-$P_3N_3F_4(C_6H_5)_2$ isomers exhibit the same distribution of ions. On the other hand, there is an interesting differential in peak intensities. The intensities of the ions in the spectrum of the *cis* isomer are generally greater than those of the *trans* isomer. The intensity of the $P_3N_3F_4C_6H_5^+$ ion, however, is significantly greater in the *trans* isomer. This observation can be interpreted as reflecting a more facile cleavage of the phosphorus–carbon bond in the *trans* compared to the *cis* isomer. We have recently discussed labilization (as reflected in ^1H n.m.r. parameters) of the phenyl group in *trans*-1,3-$P_3N_3F_4(C_6H_5)_2$.[1]

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The interpretation of the mass spectral data is consistent with our previous considerations of this effect [1] as being due either to conformational differences between *cis* and *trans* isomers or the *cis* labilizing effect of the fluorine atom.[10]

ative to the disubstituted derivatives. This trend is reasonable because in the disubstituted derivatives both electrons can be lost from the easily ionized aryl groups.

The mass spectra of the tetra-aryl fluorocyclotriphosphazene may be found in Table 4. In addition to

TABLE 2

Selected mass spectra of molecules of the type $P_3N_3F_4Ar_2$

	Relative abundance [a]				
Ions observed	*cis*-1,3-$P_3N_3F_4R_2$	*trans*-1,3-$P_3N_3F_4R_2$	1,3-$P_3N_3F_4R'_2$ [c]	1,1-$P_3N_3F_4R_2$	1,1-$P_3N_3F_4R'R''$
$P_3N_3F_4Ar_2^+$	100% (18·2%) [d]	100% (21·0%)	100%	100%	100%
$P - 14^+$ [b]	4·4 (0·81)	2·1 (0·49)	7·4		
$P - 15^+$ [b]	27·8 (4·77)	13·5 (2·67)	18		
$P - 19^+$ [b]	7·9 (1·41)	4·1 (0·89)	0·6	1·1	2·9 [e]
$P - 20^+$ [b]	12·7 (2·18)	8·5 (1·76)			1·5 [e]
$P_3N_3F_4ArC^+$	5·9 (0·74)	3·1 (0·79)		0·9	
$P_3N_3F_4Ar^+$	4·8 (1·30)	6·6 (1·35)	1·6	32·1	$P_3N_3F_4R'$ = 16·4 $P_3N_3F_4R''$ = 15·5
Miscellaneous ions	$P_3N_3C_6H_4C(?)$ 10·7 $P_3N_2F_4C_6H_4$ 3·2 $P_2NF_3C_6H_5$ 3·6	$P_3N_3F_3C_6H_4C$ 5·8 $P_3N_2F_4C_6H_4$ 2·9 $P_2NF_3C_6H_5$ 3·3	$P - 17$ 11·8 225 (*m/e*) 28·8		
$P_3N_3F_4^+$	0·8 (0·13)	3·5 (0·74)	0·4	7·3	3·2
$P_3N_2F_4^+$	34·9 (5·98)	36·4 (6·46)	10·3	4·8	5·5
$P_3N_3F_4Ar_2^{2+}$	5·0 (0·92)	4·6 (0·97)	13·9	3·1	2·1

[a] R = C_6H_5; R′ = *p*-$C_6H_4N(CH_3)_2$; R″ = C_6D_5. [b] *P* = parent ion; see text. [c] Mixture of *cis* and *trans* isomers; large series of unassigned peaks from *m/e* 285 to 421. [d] Expressed as % of total ionization. [e] Complex series from $P - 18$ to $P - 22$; abundance 1·5 to 2·9%.

TABLE 3

Selected metastable transitions

Compound	Metastable transition Observed	Calculated	Process
$P_3N_3F_5C_6D_5$	135	135·4	$P_3N_2F_5^+ \longrightarrow P_2NF_5^+ + PN$
1,3-$P_3N_3F_4(C_6H_5)_2$ [a]	326	326·1	$P_3N_3F_4(C_6H_5)_2^+ \longrightarrow P_3N_3F_3(C_6H_5)(C_6H_4)^+ + HF$
	336	335·6	$P_3N_3F_4(C_6H_5)_2^+ \longrightarrow P_3N_2F_4(C_6H_5)(C_6H_4)^+ + NH$
1,1,3,3-$P_3N_3F_2(C_6H_5)_4$	320	319·0	$P_3N_3F_2(C_6H_5)_3^+ \longrightarrow P_2N_2F_2(C_6H_5)_3^+ + PN$

[a] Both *cis* and *trans* isomers.

The spectra of the *NN*-dimethylanilino-derivatives are more difficult to interpret due to complications of aryl group fragmentation. Thus, the $P - 15$ peak can represent loss of CH_3 and/or NH (or both). The loss of fluorine atoms in these derivatives is minimal. Other features of the spectra are similar to those observed in the phenyl derivatives, *i.e.* successive loss of aryl groups is the major fragmentation route for the geminal derivative while linear ion formation is more important for non-geminal isomers. In the spectrum of the geminal derivative, $P_3N_3F_4(C_6D_5)[C_6H_4N(CH_3)_2]$, loss of the deuteriophenyl group is more favourable than loss of the *NN*-dimethylanilino-group. This observation may reflect an increased transfer of electron density from the aryl group to the phosphorus atom as a result of the electron donating properties of the *p*-*NN*-dimethylamino-group.

There is an increase in the intensities of the doubly charged ions on going from the monosubstituted derivdifluorosubstituted linear ions, there are a number of low intensity peaks (especially in the *NN*-dimethylanilino-derivative) which are not assigned. As observed

TABLE 4

Selected mass spectra of the type $P_3N_3F_2Ar_4$

	Relative abundance [a]	
Ion observed	1,1,3,3-$P_3N_3F_2R_4$	1,1,3,3-$P_3N_3F_2R'_2R''_2$ [b]
$P_3N_3F_2Ar_4^+$	100%	100%
$P_3N_3F_2Ar_3^+$	37·4	23·5 ($P_3N_3F_2R'R''_2$) 4·5 ($P_3N_3F_2R'_2R''$)
$P_2N_2F_2Ar_3^+$	5·1	
$P_3N_3F_2Ar_2^+$	7·1	0·75 ($P_3N_3F_2R''_2$) 5·4 ($P_3N_3F_2R'R''$) 4·7 ($P_3N_3F_2R'_2$)
$P_3N_3F_2Ar^+$	10·4	2·7 ($P_3N_3F_2R''$)
$P_3N_3F_2Ar_4^{2+}$	6·6	13·3
$PNAr^+$	29·8	8·5 (PNR″) 6·3 (PNR′)

[a] R = C_6H_5; R′ = C_6D_5; R″ = *p*-$C_6H_4N(CH_3)_2$. [b] Configuration at each organosubstituted phosphorus is ≡PR′R″.

for the geminal disubstituted derivatives, the fragmentation pattern of the tetraphenyl derivative consists primarily of successive loss of phenyl groups leaving the P_3N_3 ring intact. In the *NN*-dimethylanilino-derivative, either a deuteriophenyl or a *NN*-dimethylanilino-group may be lost and ions resulting from both of these processes are observed. The relative intensities show that loss of the deuteriophenyl group is much more facile than loss of the *NN*-dimethylanilino-group. The tendency to have the *NN*-dimethyl substituted aryl group more strongly bonded to the phosphorus atom which was observed for the geminal disubstituted derivative becomes more pronounced in the tetrasubstituted derivative. Further aryl-phosphorus cleavage becomes complex and since the intensities of the resulting peaks are relatively low, no further discussion will be presented. In the tetraphenyl derivative, the $C_6H_5N^+$ ion is of very low intensity and the $C_6H_5PN^+$ ion becomes significant. In the mixed *NN*-dimethylanilino–deuteriophenyl derivative, both aryl PN^+ ions are observed.

The intensities of the doubly charged ions are greater than those for the corresponding disubstituted derivatives. In part, this reflects the ability of the molecule to have the electrons lost from aryl groups on different phosphorus atoms and the decreased electron withdrawing ability [1] of the highly substituted fluorocyclotriphosphazene.

In conclusion, we have shown that there are two basic fragmentation patterns for the aryl substituted cyclotriphosphazene. The pattern which plays the dominant role is determined by which positional isomer is under investigation. Thus mass spectroscopy appears to hold promise as a structural tool in phosphazene chemistry. A variety of other processes occur in the mass spectra of these species many of which can be related to the solution chemistry of the cyclotriphosphazene derivatives.

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