Journal of Fluorine Chemistry, *30* (1985) 269–287

Received: April 29, 1985; accepted: September 19, 1985

REACTIONS OF PERFLUORONITRILES. II. INTERACTIONS WITH PHENYLPHOSPHINE

K. J. L. PACIOREK, J. H. NAKAHARA, and R. H. KRATZER

Ultrasystems, Inc., 16845 Von Karman Avenue
Irvine, California 92714 (U.S.A.)

SUMMARY

Treatment of perfluoro-n-octanonitrile with phenylphosphine gave tetraphenyltetraphosphine and a spectrum of reduction and interaction products. Fifteen compounds were identified. The imine, ($R_f=C_7F_{15}$) $R_fCH{=}NH$, and the amine, $R_fCH_2NH_2$, were the primary reduction products. Secondary phosphorus-free products, some formed following ammonia evolution, were the following: $R_fCH{=}NCH_2R_f$, $R_fCH_2CH(NH_2)R_f$, $R_fC({=}NH)N{=}CR_f(NH_2)$, $R_fCH_2NHCR_f({=}NH)$, $(R_fCN)_3$, $R_fCH{=}NCR_f{=}NCR_f({=}NH)$, $R_fCH_2N{=}CR_fNHCH_2R_f$, and $R_fCH_2N{=}CR_fNHCR_f({=}NH)$. Only three phosphorus-containing materials were definitely identified: $R_fCH(NH_2)P(C_6H_5)H$, $R_fCH[P(C_6H_5)H]N{=}CHR_f$, and $R_fC({=}NH)P(C_6H_5)CR_f({=}NH)$. Depending on reaction conditions, specific phosphorus-containing compounds could be preferentially produced. All the structure assignments are based solely on mass spectral breakdown patterns, since pure compounds were not isolated.

INTRODUCTION

Aniline was found to add readily to perfluoro-n-octanonitrile giving N-phenyl-perfluoro-n-octylamidine, N'-(perfluoro-n-octylimidoyl)-N-phenyl-perfluoro-n-octylamidine, and the corresponding diphenyl-analogues [1]. No studies have been reported in the literature on the addition reactions of phosphines to perfluorinated nitriles. Yet, based on the relative

0022-1139/85/$3.30

ease of the addition of aniline to these systems, one would expect a related behavior. Thus, in analogy to aniline, initial investigations were performed with phenylphosphine.

RESULTS AND DISCUSSION

Interactions of phenylphosphine and perfluoro-n-octanonitrile were carried out both neat and in solvents. The reactions are summarized in Table 1.

TABLE 1

Interactions of perfluoro-n-octanonitrile and phenylphosphine[a]

	Reactants		Conditions			Partial Analysis		
Test No.	ΦPH_2 mmol	$C_7F_{15}CN$ mmol	Temp °C	Time hr	Solv.	ΦPH_2[b] %	R_fCN[c] %	Φ_4P_4[b] %
1	7.42	2.40	130	15	none	40	-	29
2	2.65	7.68	130	36	none	-	51	55
3	25.43	25.36	50	654	A/F[d]	n.d.	n.d.	52
4	1.33	12.66	130	24	none	-	84	42

[a] Tests 1,2,4 were performed in sealed tubes in vacuo; test 3 was carried out under nitrogen by-pass.

[b] Based on phenylphosphine employed.

[c] Based on perfluoro-n-octanonitrile employed.

[d] A 1:1, by volume, acetonitrile/Freon mixture was utilized.

The product mix, left after removal of the volatile starting materials and the precipitated tetraphenyltetraphosphine, depended strongly on the conditions employed. This is clearly evident from the data given for Tests 1, 3, and 4 in Figs. 1-3. Under all the conditions studied, reduction was the major process. No 'primary' adduct of phenylphosphine was detected. None of the products, with the exception of $C_7F_{15}CH_2NHC(C_7F_{15})=NH$ (VII) were isolated and characterized. All of the identifications are thus based solely on mass spectrometry.

As mentioned above, reductions by phenylphosphine, with concomitant formation of tetraphenyltetraphosphine, constituted one of the major processes taking place. This is clearly evident from the high yield of the isolated tetraphenyltetraphosphine shown in Table 1. Subsequent reactions of the reduced materials with perfluoro-n-octanonitrile and with each

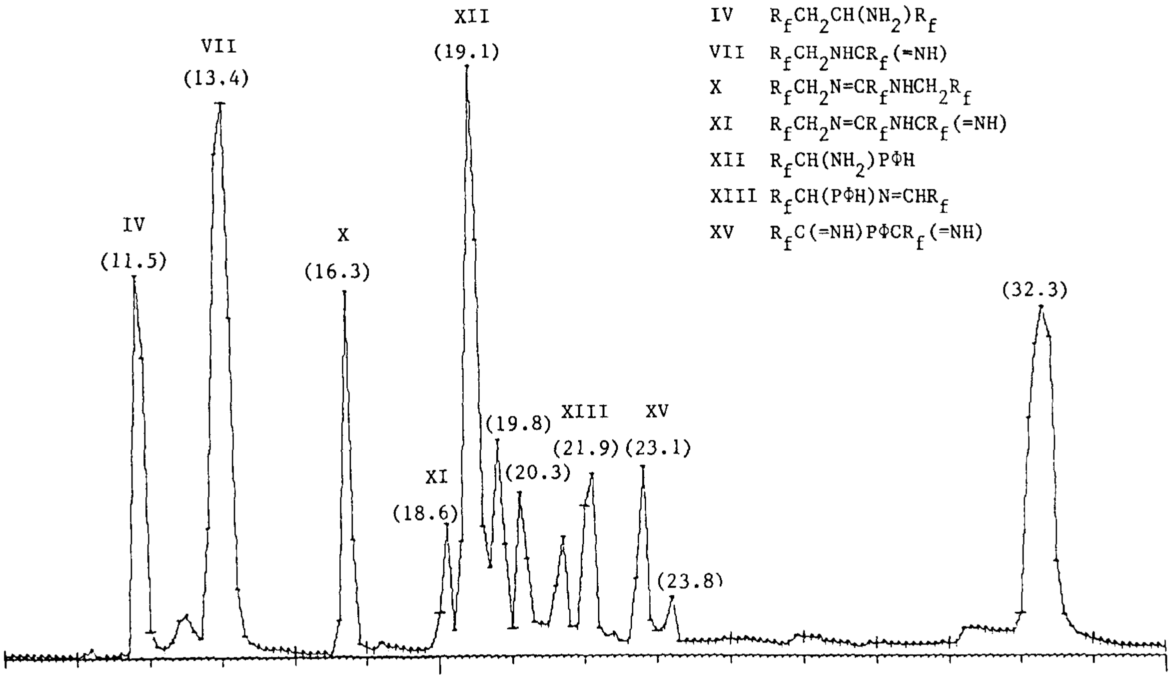


Fig. 1. Ion chromatogram of the product mix from the interaction of phenylphosphine and perfluoro-n-octanonitrile in a 3:1 mole ratio at 130°C for 15 hr (Test No. 1, Table I).

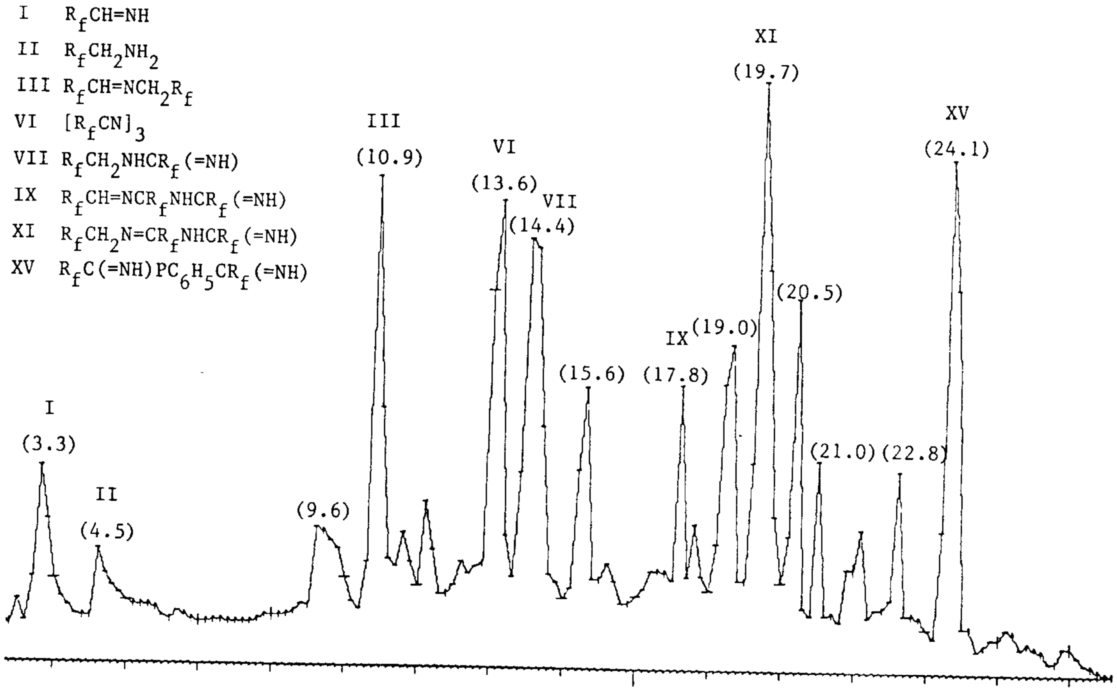
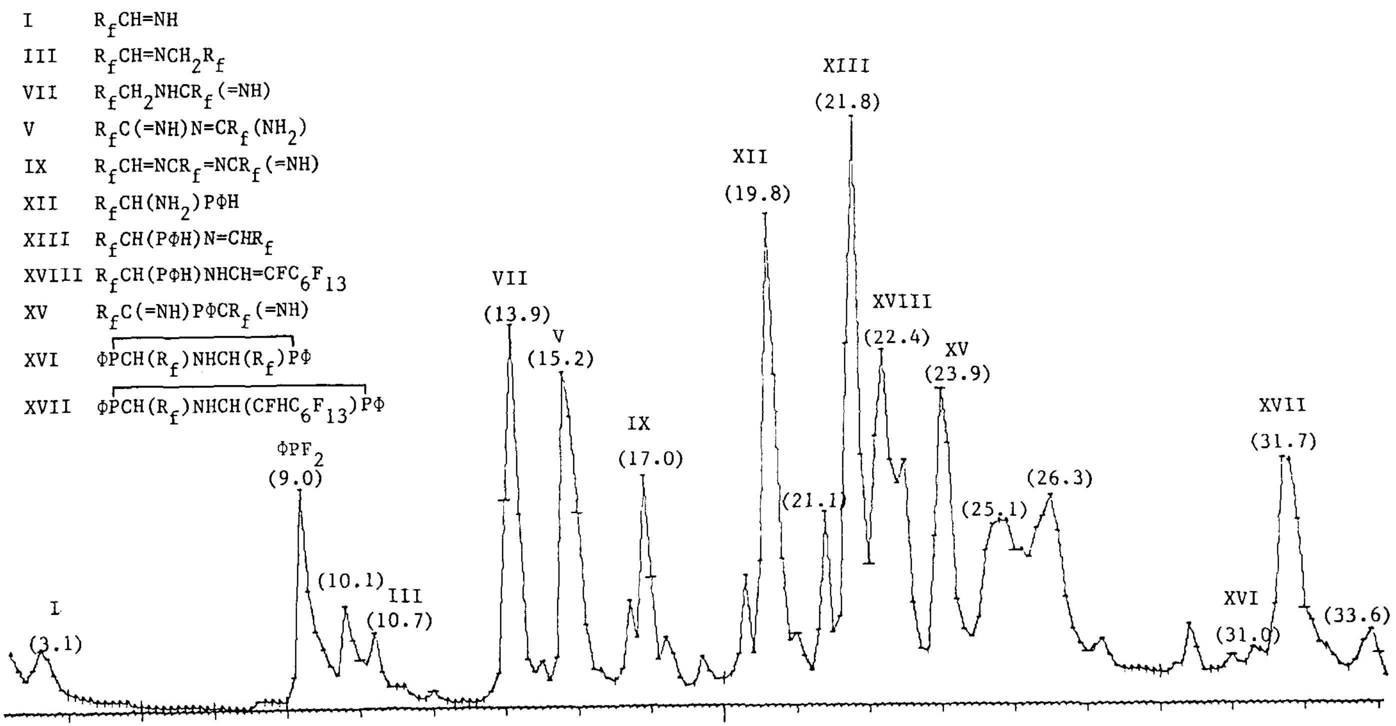


Fig. 2. Ion chromatogram of the product mix from the interaction of phenylphosphine and perfluoro-n-octanonitrile in a 1:10 mole ratio at 130°C for 24 hr (Test No. 4, Table I).



I	$R_fCH=NH$
III	$R_fCH=NCH_2R_f$
VII	$R_fCH_2NHCR_f(=NH)$
V	$R_fC(=NH)N=CR_f(NH_2)$
IX	$R_fCH=NCR_f=NCR_f(=NH)$
XII	$R_fCH(NH_2)P\Phi H$
XIII	$R_fCH(P\Phi H)N=CHR_f$
XVIII	$R_fCH(P\Phi H)NHCH=CFC_6F_{13}$
XV	$R_fC(=NH)P\Phi CR_f(=NH)$
XVI	$\Phi PCH(R_f)NHCH(R_f)P\Phi$
XVII	$\Phi PCH(R_f)NHCH(CFHC_6F_{13})P\Phi$

Fig. 3. Ion chromatogram of the product mix from the interaction of phenylphosphine and perfluoro-n-octanonitrile in a 1:1 mole ratio at 50°C for 27 days (Test No. 3, Table I).

other gave rise to the wide spectrum of products found. A number of the reactions were accompanied by evolution of ammonia. This is proven by the nature of the compounds, formation of triazine, VI, and in particular the presence of imidoylamidine, V [2].

The relatively simple products and the potential paths for their formation are presented in Table 2. The undetected, plausible compounds are those shown in brackets. Only three of the compounds listed were the adducts of phenylphosphine. Yet, under specific conditions, the individual compounds could be obtained in relatively good yields. For example, the yield of the phenylphosphine-dinitrile adduct, XV, increased from ∿3% to 28% by changing the nitrile to phenylphosphine ratio from 0.3 to 10. It is believed that tailoring further the reaction conditions should permit its actual isolation.

The presence of solvent seemed to affect strongly the type of products formed. The production of the more complex compounds was kinetically controlled. This is clearly evident from the plots given in Fig. 4. Initially at 50°C in acetonitrile/Freon-113 solvent mixture, the only material present to a significant degree was the reduced phenylphosphine adduct XII. However, as time progressed, the secondary or rather tertiary products started to appear. The complexity of the product mix after 654 hr (27 days) exposure is illustrated by the ion chromatogram presented in Fig. 3. It should be pointed out that in the ion chromatogram the concentration of compound XIII appears to be higher than that of XII; however, the opposite is true using flame ionization, which is believed to be much more reliable in concentration determinations.

Compounds XVIII, XVI, and XVII have not been detected in the tests performed in the absence of solvent. The material with a retention time of 32.3 min in Fig. 1 has not been identified; it does, however, contain one or more phenylphosphine substituents. Regarding compound XVI, it could be formed by either of the paths delineated on page 277.

TABLE 2

Compilation of reactions leading to specific products obtained on interaction of phenylphosphine and perfluorooctanonitrile[a]

$$R_fCN + C_6H_5PH_2 \longrightarrow \underset{\text{I}}{R_fCH{=}NH} + \tfrac{1}{4}(C_6H_5P)_4$$

$$R_fCN + 2\,C_6H_5PH_2 \longrightarrow \underset{\text{II}}{R_fCH_2NH_2} + \tfrac{1}{2}(C_6H_5P)_4$$

$$\underset{\text{I}}{R_fCH{=}NH} + \underset{\text{II}}{R_fCH_2NH_2} \longrightarrow \underset{\text{III}}{R_fCH{=}NCH_2R_f} + NH_3$$

$$2\,\underset{\text{II}}{R_fCH_2NH_2} \longrightarrow \underset{\text{IV}}{R_fCH_2CH(NH_2)R_f} + NH_3$$

$$2\,R_fCN + NH_3 \longrightarrow \underset{\text{V}}{R_fC({=}NH)N{=}CR_f(NH_2)}$$

$$R_fCN + NH_3 \longrightarrow \underset{\text{VI}}{1/3(R_fCN)_3} + NH_3$$

$$\underset{\text{II}}{R_fCH_2NH_2} + R_fCN \longrightarrow \underset{\text{VII}}{R_fCH_2NHCR_f({=}NH)}$$

$$\underset{\text{I}}{R_fCH{=}NH} + R_fCN \longrightarrow \underset{\text{VIII}}{\{R_fCH{=}NCR_f({=}NH)\}},\ \text{n.i.}^{b}$$

$$\underset{\text{I}}{R_fCH{=}NH} + 2\,R_fCN \longrightarrow \underset{\text{IX}}{R_fCH{=}NCR_f{=}NCR_f({=}NH)}$$

$$\underset{\text{VII}}{R_fCH_2N{=}CR_f(NH_2)} + \underset{\text{II}}{H_2NCH_2R_f} \longrightarrow \underset{\text{X}}{R_fCH_2N{=}CR_fNHCH_2R_f} + NH_3$$

$$\underset{\text{VII}}{R_fCH_2N{=}CR_f(NH_2)} + R_fCN \longrightarrow \underset{\text{XI}}{R_fCH_2N{=}CR_fNHCR_f({=}NH)}$$

$$\underset{\text{I}}{R_fCH{=}NH} + C_6H_5PH_2 \longrightarrow \underset{\text{XII}}{R_fCH(NH_2)P(C_6H_5)H}$$

$$\underset{\text{XII}}{R_fCH(NH_2)P(C_6H_5)H} + HN{=}CHR_f \longrightarrow \underset{\text{XIII}}{R_fCH[P(C_6H_5)H]N{=}CHR_f} + NH_3$$

$$R_fCN + C_6H_5PH_2 \longrightarrow \underset{\text{XIV}}{\{R_fC[P(C_6H_5)H]{=}NH\}},\ \text{n.i.}$$

$$2\,R_fCN + C_6H_5PH_2 \longrightarrow \underset{\text{XV}}{R_fC({=}NH)P(C_6H_5)CR_f({=}NH)}$$

---

[a] R_f corresponds to C_7F_{15}.

[b] Not identified.

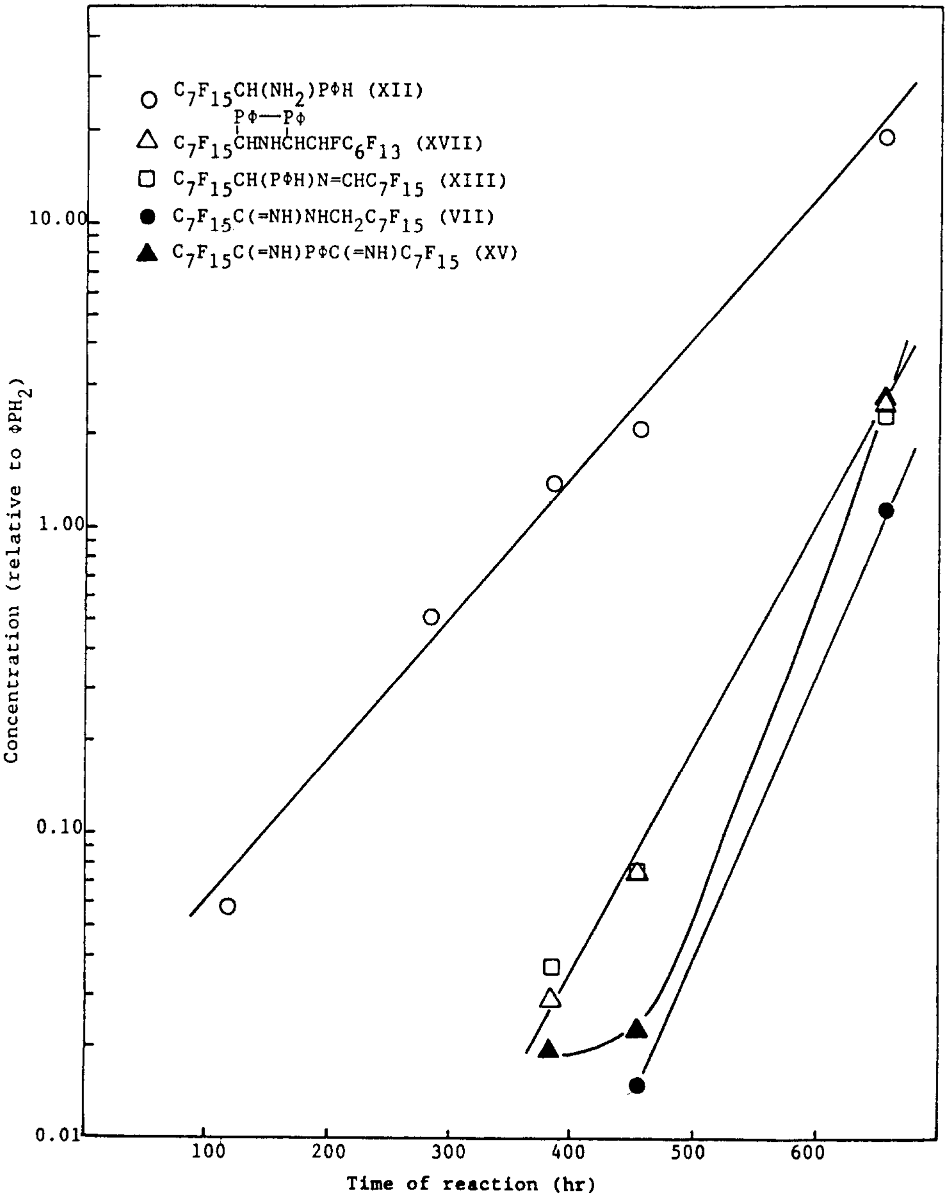
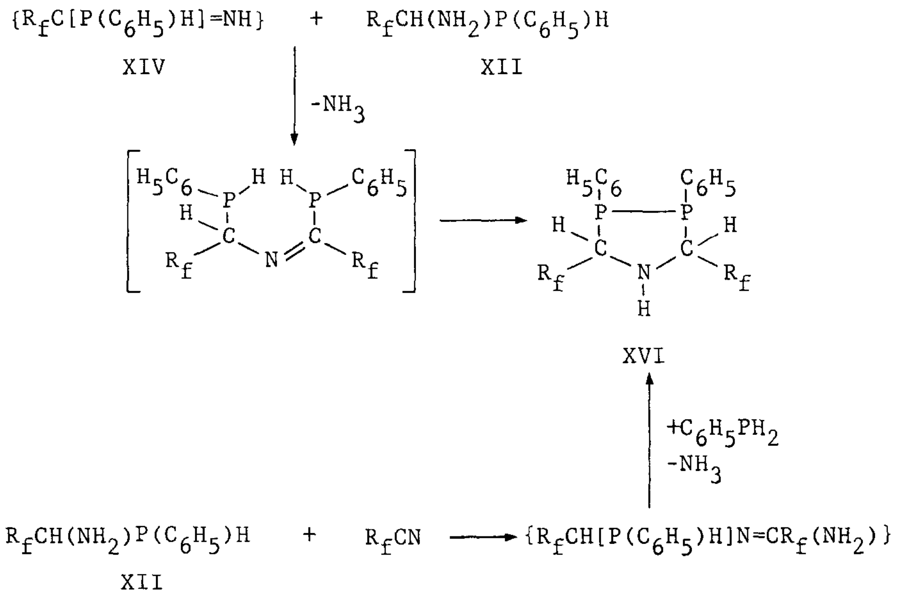


Fig. 4. Semi-log plot of concentration versus time for products from the reaction of phenylphosphine and perfluoro-n-octanonitrile at 50°C in acetonitrile/Freon-113



The mass spectral assignments for the majority of the compounds listed in Table 2 will be discussed later. These are straightforward inasmuch as the structures involved are reasonably simple. Structural assignment for XVI is, however, definitely more complex. Here, the intense ions in the high mass region presented in Table 3 are fully supportive of the postulated structure. The m/e 995 is the molecular ion. Loss either from this ion or from the neutral molecule of a fluorine atom gives m/e 976, whereas the loss of the C_7F_{15} side chain gives the 626^+ ion. The subsequent loss of CH=NH moiety, 598^+, confirms the $R_fCH\text{-}NH$ arrangement. The presence of the diphosphine unit $C_6H_5PPC_6H_5$ is proven by the ions 460^+, 410^+, and 390^+, i.e.,

$$M(995) \longrightarrow 460^+ + 535\ [C_6H_5PPC_6H_5 + C_6F_{13}]$$

$$M(995) \longrightarrow 410^+ + 585\ [C_6H_5PPC_6H_5 + C_7F_{15}]$$

$$M(995) \longrightarrow 390^+ + 605\ [C_6H_5PPC_6H_5 + C_7F_{15} + HF]$$

as well as the $C_6H_5PPC_6H_5(H)^+$, m/e 217, and the $C_6H_5PPC_6H_5{}^+$, m/e 216, ions.

TABLE 3

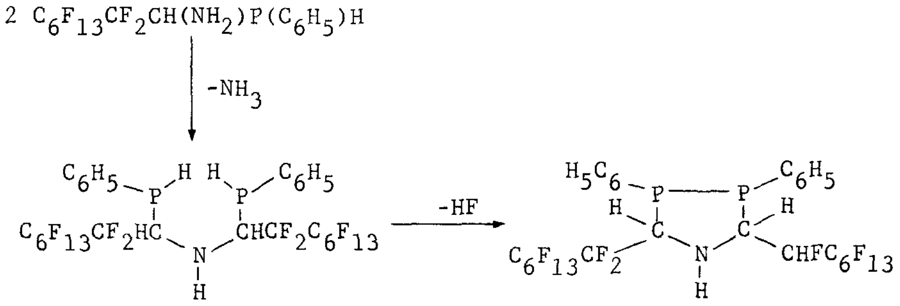
Mass spectral breakdown patterns of $\Phi \overline{PCH(C_7F_{15})NHCH(C_7F_{15})P}\Phi$ (XVI), $\Phi \overline{PCH(C_7F_{15})NHCH(CFHC_6F_{13})P}\Phi$ (XVII), and $C_7F_{15}CH(P\Phi H)N{=}CHCFHC_6F_{13}$ (XVIII)[a]

m/e	XVI	XVII	XVIII	m/e	XVI	XVII	XVIII	m/e	XVI	XVII	XVIII
28	24.2	18.7	13.0	151	8.3	7.1	3.3	490	3.1		4.0
31	5.6	5.4	5.8	152	6.5	5.5	3.1	491			8.1
39			4.8	153	3.1	10.2	9.5	492			5.9
50	5.6	3.7	4.9	154	3.3	7.9		497	5.9		
51	12.3	9.7	9.3	157	3.9	4.2		504	3.4		
57	4.6	3.2	6.9	164		3.0		505	4.7		
65			9.8	165	4.4	5.1		550			9.8
69	28.0	21.5	22.6	169	4.6	3.1	3.7	580		17.8	
72		8.6	23.3	171	22.7	13.0	16.2	581		6.8	
75	4.0	4.4		172	10.7	4.4	4.9	598	17.7	17.4	
76		3.1		173			8.1	599	6.3	5.7	
77	24.0	17.0	5.9	181	3.0	3.8		608		18.3	
78	6.7	5.8	6.0	182	3.2	3.6		609		4.8	
79	3.3			183	34.6	25.1		626	35.1	12.0	
81	5.7	4.1	4.6	184	7.6	7.8		627	12.1	3.9	
83	3.2		9.9	185	$\underline{100.0}$	81.9		710			4.1
90	14.6	8.7	18.3	186	23.3	22.1		722			13.6
95		4.3	3.6	187		3.2		723			4.1
96			3.8	214	3.2			742		5.7	3.5

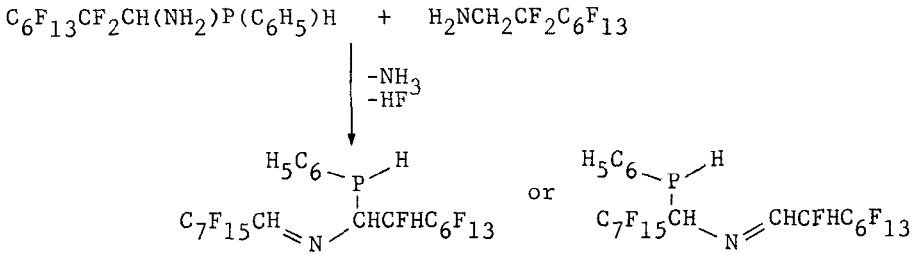
100	6.2	5.7	6.0	216	24.1	11.3		760	9.7	7.5	100.0
102	4.3	3.2		217	49.1	39.4		761			30.7
107	23.8	19.7	15.3	218	10.1	9.6		762			4.2
108	22.8	19.1	17.1	222			6.4	829			3.0
109	17.3	15.7	56.6	229	19.3	17.3		831			5.5
110	3.2		13.7	230	4.0	3.4		850			13.1
113	4.1	3.4	4.4	235		3.7		851			3.8
119	8.4	6.4	7.5	240			4.1	868		3.7	
121	5.7	3.0	5.0	372		4.3	7.3	869		4.2	56.9(M^+)
122			4.3	390	10.2	3.9	7.2	870			17.8
123		18.6		392		3.6	3.6	871			3.0
127	42.7	39.5	36.2	410	10.1	4.2		917	3.5		
128	6.6	6.4	8.2	442		22.8		958		24.1	
131	8.1	5.9	6.1	443		3.0		959		11.8	
133	4.1	5.3		460	26.9			976	27.0	8.0	
134		3.4	3.7	461	5.6			977	9.3	100.0(M^+)	
136	3.5			468		4.8		978		36.7	
138	22.2	15.1		472		5.3	11.1	979		8.5	
139	48.1	39.9		486	5.8	3.7		995	98.2(M^+)	5.1	
140	7.9	8.7	7.4	487		6.3		996	35.3		
141	23.3	3.1	3.3	488		7.3		997	8.9		
146		3.5	3.2								

[a] Peaks having intensities lower than 3% of the base peak are not reported.

The origin of compounds XVII and XVIII is more obscure than that of XVI. Yet, the paths leading to the two materials must be related. Potential mechanisms are depicted below:



XVII



XVIIIa

or

XVIIIb

It must be understood that both the proposed mechanisms and structural arrangements are highly speculative; however, at least in the case of compound XVII, the structural assignment based on the fragmentation pattern given in Table 3, is well grounded. This is true both with respect to breakdown pattern similarity to that of compound XVI, discussed above, as well as with respect to the GC retention time.

In analogy to compound XVI, this material also exhibits in its mass spectrum a very intense molecular ion, 977^+, which here actually constitutes the base peak. Loss of fluorine then gives the 958^+ ion. However, of particular interest here are the ions m/e 626^+, 608^+, 598^+, and 580^+, which correspond to the loss of either of the two side chains, namely C_7F_{15} and $CHFC_6F_{13}$, and thus confirm the proposed arrangement, i.e.:

$$M(977) \longrightarrow 626^+ \quad + \quad 351\ [CFHC_6F_{13}]$$
$$M(977) \longrightarrow 608^+ \quad + \quad 369\ [C_7F_{15}]$$
$$M(977) \longrightarrow 598^+ \quad + \quad 379\ [CFHC_6F_{13} + CH{=}NH]$$
$$M(977) \longrightarrow 580^+ \quad + \quad 397\ [C_7F_{15} + CH{=}NH]$$

In the same manner as in compound XVI, here also the presence of the diphosphine unit, $C_6H_5PPC_6H_5$, is shown by the ions $422^+[M - C_6H_5PPC_6H_5 - C_6F_{13}]$, $229^+[(C_6H_5)PP(C_6H_5)CH]$, $217^+[C_6H_5PPC_6H_5(H)]$, and $216^+[C_6H_5PPC_6H_5]$.

Regarding compound XVIII, unfortunately the fragmentation pattern does not provide sufficient information to completely support or eliminate from consideration either structure XVIIIa or XVIIIb. The ion $760^+[M - 109(C_6H_5PH)]$, which constitutes the base peak, does prove the presence of C_6H_5PH substituent, whereas the ion $472^+[M - 397(C_7F_{15} + CH{=}NH)]$ tends to indicate that C_6H_5PH is located on the carbon to which is attached the $CFHC_6F_{13}$ side chain. On the other hand, the $491^+[M - 378(C_7F_{14} + CH{=}NH)]$ ion would favor the arrangement XVIIIb.

The mass spectral breakdown patterns of the relatively simple compounds which are listed in Table 1 are compiled in Tables 4-6. The isomerism due to proton location is to be expected with analogy to the amidine and imidoylamidine type of arrangements derived from interactions of ammonia and perfluoroalkyl nitriles. Thus, for instance, VII can be depicted in either form:

$$R_fCH_2NHC(R_f){=}NH \rightleftharpoons R_fCH_2N{=}C(R_f)NH_2$$

This, however, will not affect the fragmentation patterns and for ease of presentation, only one form has been used.

In Table 4 are compiled mass spectral data for perfluoro-n-octanonitrile reduction and interaction compounds. Although no molecular ions were registered for the two primary nitrile

TABLE 4

Mass spectral breakdown patterns of $R_fCH{=}NH$ (I), $R_fCH_2NH_2$ (II), $R_fCH{=}NCH_2R_f$ (III), and $R_fCH_2CH(NH_2)R_f$ (IV)[a]

m/e	I	II	III	IV	m/e	I	II	III	IV
27	3.4				131	40.5	11.8	10.8	3.4
28	100.0		16.5		133			4.5	
29	9.1	4.6			159	4.7			
30		100.0			169	11.3		6.8	
31	8.2	9.9	3.0		181	8.2	3.7		
41			5.4		207	3.1			
43			4.0		281	4.9	4.3		
46	3.2				298		4.8		
50	9.5	3.3			308	5.5			
51	13.0		14.4		328	5.9			
61		28.4			348		18.2		
64			4.9		358	7.3			
69	48.4	19.4	33.2	8.5	360		3.4		
77	5.6				378	44.0			
78	25.9	9.3			379	7.4			
79		24.4			380		55.8		
80		15.0			381		7.8		
81	5.6	4.2			397		4.2		
83			5.4		398	5.0	28.6		
90			16.3		399		3.4(M^+)		
91			7.8		410			100.0	8.2
92				5.9	411			14.7	
93	8.3	3.3			412				100.0
95			6.1		413				14.2
100	26.6	13.3	6.6		460			4.4	
108	7.5				462				3.5
110		8.4			760			25.5	
112	3.4				761			5.5	
113	7.8				762				24.7
119	19.6	6.3	10.9		763				3.2
122			3.6		780				4.3
128	6.5								

[a] Peaks having intensities lower than 3% of the base peak are not reported; R_f is C_7F_{15}.

reduction products, $C_7F_{15}CH{=}NH$, I, and $C_7F_{15}CH_2NH_2$, II, the presence in the mass spectrum of $C_7F_{15}CH{=}NH$ of 378^+[M - 19(F)], 78^+[$CF_2CH{=}NH$], and 28^+[CH=NH], supported by the GC retention time, proves the composition beyond any doubt. The same applies to $C_7F_{15}CH_2NH_2$, II, based on 398^+[M - 1(H)], 380^+[M - 19(F)], 79^+[CF_2CHNH_2], and 30^+[CH_2NH_2]. Material III also did not form a molecular ion; however, its breakdown pattern was in total agreement with the structural assignment, *i.e.*, 760^+[M - 19(F)], 410^+[M - 369(C_7F_{15})], and 28^+[CH=NH]. Only a very

TABLE 5

Mass spectral breakdown patterns of $R_fCH_2NHCR_f(=NH)$ (VII), $R_fCH_2NHC(R_f)=NCH_2R_f$ (X), $R_fCH_2NHC(R_f)=NCR_f(=NH)$ (XI), and $R_fCH=N-C(R_f)=NC(=NH)R_f$ (IX)[a]

m/e	VII	X	XI	IX	m/e	VII	X	XI	IX
31	3.1			3.8	476	10.0			
41				3.5	487		5.2		
43	5.0				498				12.0
51		7.3	4.6		499				7.8
53				3.3	500			5.3	
55	9.7	7.9	5.8		501			3.7	
68			4.3		505	10.2			
69	26.3	26.4	25.8	36.7	530				4.6
76				7.9	719		4.0		
77				3.9	755	6.8			
78	3.6		5.9		761			3.9	
79	3.1				773				3.3
83		3.2			774	6.4			
86	4.8				775	38.1		3.8	
90		5.3	3.2		776	9.5			
95		6.0			778		34.9	22.6	
100	7.4	6.1	6.4	7.7	779		8.8	5.6	
105	4.6				780			3.5	
108			3.1	3.1	787		3.1		
110	7.8				794	23.7(M^+)			
119	11.1	12.3	10.9	15.5	795	6.5			
126				3.8	797				12.6
131	10.1	9.7	8.1	15.2	798				7.5
156	3.0				799				8.6
169	8.1	13.4	7.2	10.6	800			5.6	
181	3.0		3.0	5.1	801			4.4	
182			4.8		805		3.7		
219		6.2			807		100.0		
269		3.7			808		28.4		
360	3.3				809		4.3		
376				3.3	818			20.6	100.0
380	5.5				819			7.1	34.3
396	4.3		4.5	4.5	820			100.0	6.0
398	3.9		4.0		821			42.3	
405	5.9				822			6.4	
410		7.8			857		42.0		
425	100.0		8.5		858		12.6		
426	17.4				866				17.8
437		10.3			867				7.8
450			4.4		868				3.7
455	12.6				870			3.0	
458		3.2		3.2	1007		3.4		
475	48.0		3.0						

---

[a] Peaks below m/e 31 and of intensities lower than 3% of the base peak are not reported; R_f is C_7F_{15}.

TABLE 6

Mass spectral breakdown patterns of $R_fCH(NH_2)P\Phi H$ (XII), $R_fCH(P\Phi H)N{=}CHR_f$ (XIII), and $R_fC({=}NH)P\Phi CR_f({=}NH)$ (XV)[a]

m/e	XII	XIII	XV	m/e	XII	XIII	XV
28	47.1	14.2	9.0	169		9.0	7.8
31	3.2	3.7	3.0	171	3.5	28.6	
39	5.9	3.7		172		4.4	
46			3.1	173		7.0	
50	4.5	5.1	4.1	190		3.1	
51	9.2	10.6	5.1	212			9.1
56	3.4			240		5.9	
57	7.1	5.0		290		3.6	
60	3.3			298	4.9		
65	8.6	7.1		348	28.0		
66	5.9			349	4.0		
69	17.3	43.4	28.0	378	5.5		
75		3.5		379	10.7		
77	7.1	9.6	8.6	390		12.5	
78	11.1	6.4	6.0	398	100.0		
79	36.5	3.0		399	17.7		
80	4.3			410		10.0	
81	6.1	4.9	4.0	490		14.9	
83	9.5	10.1		491		6.6	
90		31.7		498		3.5	
96		3.7		501		16.7	
100	7.4	9.2	6.1	502		3.1	
104			3.1	504			3.5
107	18.0	15.8	26.4	507	11.0(M^+)		
108	32.4	11.1	100.0	508	3.1		
109	27.3	100.0	19.8	531			85.4
110	80.1	13.2		532			23.2
111	12.5			568		10.3	
113		4.8		569		3.0	
119	5.9	12.0	12.4	581			4.1
121		5.1		778		51.5	
127	18.0	42.5	39.8	779		15.6	
128	4.7	6.9	5.8	780		3.2	
129	6.5			868		6.3	
131	9.3	13.8	8.5	869		3.4	
135			6.7	870		3.5	
136			6.4	881			29.8
138	3.5			882			9.2
140		5.6		887		24.3(M^+)	
143		7.4	5.0	888		6.1	
146		3.1	6.2	900			62.5(M^+)
151		3.8		901			19.9
152		3.2		902			3.2
165			7.7				

[a] Peaks having intensities lower than 3% of the base peak are not reported; R_f is C_7F_{15}.

low intensity (1.1%) molecular ion, 781^+, was registered for $C_7F_{15}CH(NH_2)CH_2C_7F_{15}$, but again the fragmentation pattern 762^+[M - 19(F)], 412^+[M - 369(C_7F_{15})] confirmed the structural arrangement.

The presence of a molecular ion facilitates greatly structural determination. In the group listed in Table 5, this applied only to $C_7F_{15}CH_2NHC(C_7F_{15})=NH$. Here the composition could be easily deduced from the ions: 794^+[M], 775^+[M - 19(F)], 475^+[M - 319(C_6F_{13})], and 425^+[M - 369(C_7F_{15})]. However, in the case of the other compounds such as X, molecular weight 1176, beyond the mass spectrometer/computer range of m/e 1066, assignment was based both on GC retention times and the characteristic fragmentation patterns. In this type of compound, the breakdown is dominated by the loss of the C_7F_{15} side chain shown here by the 807^+ ion. The same applies to compound XI, molecular weight 1189, where again the base peak, m/e 820, was formed by the loss of the perfluoroheptyl chain. Similar reasoning led to the identification of compound IX of molecular weight 1187. Here the 818^+ ion corresponded to the loss of the C_7F_{15} chain.

The products containing the C_6H_5P moiety, which are presented in Table 6, all had molecular weights within the range of the mass spectrometer system. Furthermore, each material did form a relatively high intensity molecular ion. This made the composition determination relatively easy. In all the adducts, it is postulated that phosphorus resides on carbon not nitrogen. This is based primarily on our work with diphenylphosphine which is to be reported later.

The fragmentation pattern of $C_7F_{15}CH(NH_2)P(C_6H_5)H$, XII, namely the molecular ion 507^+, 398^+[M - 109(P(C_6H_5)H)], 110^+ [P(C_6H_5)H_2], 79^+(CF_2CHNH_2], and 28^+[CH=NH], are fully consistent with the postulated arrangement. The same applies to compound XIII, *i.e.*, 887^+[M], 868^+[M - 19(F)], 778^+[M - 109(P(C_6H_5)H)], 568^+[M - 319(C_6F_{13})], 501^+[M - 386(C_7F_{15} + NH_3)], 490^+[M - 397(C_7F_{15} + CH=NH)], 410^+[M - 477(C_7F_{15} + PC_6H_5)], 109^+[P(C_6H_5)H], 90^+[CF_2CH_2CN], and 28^+[CH=NH]. With respect to the location of the P(C_6H_5)H group on carbon not nitrogen, the ions 501^+ and 490^+ support strongly the structure proposed.

Compound XV has a completely different arrangement from the previous two materials. Again, the fragmentation is in total agreement. Ions 900^+[M], 881^+[M - 19(F)], and 531^+[M - 369(C_7F_{15})], although in support of the structure, do not really confirm it. However, the absence of the M - P(C_6H_5) or M - P(C_6H_5)H ions, in conjunction with the base peak at m/e 108^+[C_6H_5P] and the presence of the 135^+ ion [$C_7F_{15}C{=}NH$], absent in compounds XII and XIII, prove the validity of the postulated arrangement. It should be noted that the infrared spectrum of the product mixture containing 50% of compound XV provided further proof of the structure, based on the absence of P-H absorption at 2300 cm^{-1}.

EXPERIMENTAL

The general experimental procedures employed were the same as described in Part I of the series [1].

In the sealed tube experiments, the reactants were introduced into the ampoule using a vacuum line assembly. Subsequently, the ampoule was sealed in vacuo and exposed to a selected temperature for a denoted period of time as given in Table 1. After conclusion of heating, the ampoule was opened to the vacuum system and the volatiles were fractionated from a warming trap through traps held at -23 and -78°C into a liquid nitrogen cooled trap. The separated condensibles, largely phenylphosphine and perfluoro-n-octanonitrile, were then quantitated. The involatile residue was taken up in Freon-113 to remove and quantitate the tetraphenyltetraphosphine; the residue left after solvent removal was analyzed by combined gas chromatography/mass spectrometry (GC/MS). In Test 1, Table 1, $C_7F_{15}C(NH_2){=}NCH_2C_7F_{15}$, mp 101-102°C, was isolated by sublimation. Calcd. MW, 794.18. Found, 764 (osmometry).

The experiments where solvent was utilized were performed under nitrogen by-pass. The reaction was monitored by removing aliquots for GC/MS analysis. At the conclusion of the test, the precipitated tetraphenyltetraphosphine was removed and the product mixture, after solvent removal, was subjected to GC/MS analysis. Separations using fractional distillation were unsuccessful in material isolation.

ACKNOWLEDGEMENTS

Research sponsored by the Air Force Office of Scientific Research (AFSC), United States Air Force, under Contract F49620-82-C-0021. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation hereon. The authors are indebted to Dr. A. J. Matuszko for helpful discussions and suggestions.

REFERENCES

1 Part I., K. J. L. Paciorek, J. H. Nakahara, and R. H. Kratzer, J. Fluorine Chem., 30 (1985) 241.
2 H. C. Brown and P. D. Schuman, J. Org. Chem., 28, 1122 (1963).