[CONTRIBUTION FROM THE U. S. NAVAL ORDNANCE LABORATORY, CORONA, CALIFORNIA]

Synthesis of Bis-(perfluoroalkyl)-phosphonitriles

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The synthesis of trimeric, tetrameric and polymeric bis-(trifluoromethyl)-phosphonitriles, $[(CF_3)_2PN]_{3,4,n}$, and of trimeric bis-(heptafluoropropyl)-phosphonitrile, $[(C_3F_7)_2PN]_3$, is accomplished by chlorination of bis-(trifluoromethyl)-phosphinous amide, $(CF_3)_2PNH_2$, and bis-(heptafluoropropyl)-phosphinous amide, $(C_3F_7)_2PNH_2$, followed by dehydrohalogenation with a tertiary amine. Evidence of the formation of the intermediate bis-(trifluoromethyl)-dichlorophosphinic amide $(CF_3)_2P(Cl_2)NH_2$ is obtained by cleavage of the P–NH_2 bond with HCl to form trichlorobis-(trifluoromethyl)-phosphorane $(CF_3)_2PCl_3$.

The reaction of dialkyl and diaryl phosphorus trichloride with either ammonia or ammonium chloride has been the object of extensive investigations, and the preparation of alkyl and aryl phosphonitriles by this procedure has been reported.[1–3] The mechanism of this reaction also has been investigated, and evidence has been obtained for the formation of intermediate compounds containing P–Cl and N–H groups.[4,5] Dehydrohalogenation of these intermediate compounds leads to the formation of the desired phosphonitrilic derivatives.

The same synthetic approach has been attempted for the preparation of bis-(trifluoromethyl)-phosphonitriles[6]; however, the desired final products were not formed. Extensive decomposition of the trichlorobis-(trifluoromethyl)-phosphorane, $(CF_3)_2PCl_3$, was observed, along with the formation, among other products, of a large amount of trifluoromethane, which indicates that ammonolysis of the carbon–phosphorus bond occurs, probably as a consequence of the highly electronegative character of the trifluoromethyl group. A polymeric material having the composition $[(CF_3)_2PN]_n$ has been obtained[7] by thermal decomposition of bis-(trifluoromethyl)-phosphinous azide, $(CF_3)_2PN_3$. The formation was observed of a very small amount of a crystalline material which was separated by vapor-phase chromatography into two fractions melting at 64° and 109°, respectively. The yield, however, was insignificant, and no further characterization was attempted.

Bis-(perfluoroalkyl)-phosphonitriles have now been obtained by chlorination of bis-(perfluoroalkyl)-phosphinous amides, $(R_F)_2PNH_2$, to form bis-(perfluoroalkyl)-dichlorophosphinic amides, $(R_F)_2P(Cl_2)NH_2$, and the subsequent dehydrohalogenation of these compounds. Chloroform and carbon tetrachloride were found to be suitable solvents for the chlorination reaction. The dehydrohalogenation was achieved by use of a nonprotonic base (*i.e.*, a tertiary amine) to avoid cleavage of the carbon–phosphorus bond.

The mechanism of this synthesis can be expressed by the equations

$$(R_F)_2PNH_2 + Cl_2 \longrightarrow (R_F)_2P(Cl_2)NH_2 \qquad (1)$$

$$(R_F)_2P(Cl_2)NH_2 + 2NR_3 \longrightarrow (R_F)_2PN + 2NR_3{\cdot}HCl \qquad (2)$$

where $R_F = CF_3$ and C_3F_7.

A reported attempt[8] to chlorinate bis-(trifluoromethyl)-phosphinous amide, $(CF_3)_2PNH_2$ (I), by use of Cl_2 in the absence of solvent failed to provide evidence for the formation of bis-(trifluoromethyl)-dichlorophosphinic amide, $(CF_3)_2P(Cl_2)NH_2$ (II). It was found, however, that a chloroform solution of I at −30° reacts smoothly with an equimolar amount of chlorine, turning the solution pale yellow with no formation of precipitate. When the solution was warmed at room temperature, extensive decomposition occurred, which made it difficult to isolate and characterize the reaction products. However, when the chloroform solution, at −30°, was treated with an excess of anhydrous HCl after the chlorination was completed, an 88% yield of trichlorobis-(trifluoromethyl)-phosphorane, $(CF_3)_2PCl_3$, and 93% of ammonium chloride, calculated on the basis of the starting compound I, were obtained according to

$$(CF_3)_2P(Cl_2)NH_2 + 2HCl \longrightarrow (CH_3)_2PCl_3 + NH_4Cl \qquad (3)$$

thus providing unequivocable evidence for the formation and composition of compound II.

Treatment of a chloroform solution of II with trimethylamine resulted in a rapid reaction and formation of a white precipitate. From the resulting mixture were isolated two volatile crystalline compounds melting at 64° and 109°. Elemental analysis and molecular weight determinations proved these two compounds to be $[(CF_3)_2PN]_3$ (m.p. 64°) and $[(CF_3)_2PN]_4$ (m.p. 109°).

A white solid nonvolatile material, insoluble in common organic solvents, was recovered from the residue after removal of the trimethylamine hydrochloride. The elemental analysis of this compound proved the composition $(CF_3)_2PN$. The X-ray diffraction patterns show that this material possesses a much lower degree of crystallinity than the trimeric and tetrameric forms. A polymeric structure is therefore postulated.

Trimeric bis-(heptafluoropropyl)-phosphonitrile, $[(C_3F_7)_2PN]_3$, was obtained in 70% yield by using bis-(heptafluoropropyl)-phosphinous amide as a starting compound and employing the same synthetic method previously described. No tetrameric homolog was recovered—only a certain

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(6) C. P. Haber and A. J. Bilbo, WADC Technical Report 56-376.

(7) G. Tesi, C. P. Haber and C. M. Douglas, *Proc. Chem. Soc.* (London) 219 (1960).

(8) G. S. Harris, *J. Chem. Soc.*, 512 (1958).

amount of an oily material whose identity has not yet been established.

The infrared absorption data for all these compounds are listed in Table I. The absorption bands for the P–N ring vibrations have been tentatively assigned. Strong shifting of these bands toward higher frequencies was noted, as compared with equivalent data for other phosphonitrilic compounds.[9,10] This result is, however, consistent with the effect of the strongly electronegative perfluoroalkyl groups on the P–N cyclic system. It is interesting to note the similarity in position between the P–N ring vibration peaks of the $[(CF_3)_2PN]_3$ (1300 cm.$^{-1}$) and the $(PNF_2)_3$ (1297 cm.$^{-1}$).[11] The same similarity exists between $[PN(CF_3)_2]_4$ (1412 cm.$^{-1}$) and $(PNF_2)_4$ (1419 cm.$^{-1}$).[11]

Experimental

Materials.—Bis-(trifluoromethyl)-phosphinous amide, $(CF_3)_2PNH_2$, and bis-(heptafluoropropyl)-phosphinous amide, $(C_3F_7)_2PNH_2$, were prepared as previously described.[8,12] The purity of these compounds was determined by gas chromatography and infrared spectroscopy. Chlorine was purified by passage, in succession, through a water scrubber, concentrated H_2SO_4 and a heater maintained at 350°. Trimethylamine was purified by contact with P_4O_{10}. All reactions were run under a blanket of dry nitrogen to prevent contamination by air and moisture.

Bis-(trifluoromethyl)-phosphonitriles, $[(CF_3)_2PN)]_{3,4,n}$.—A solution containing 37.0 g. (0.2 mole) of $(CF_3)_2PNH_2$ in 300 ml. of chloroform was cooled at −40° and under vigorous stirring was treated with 14.2 g. (0.2 mole) of chlorine. The addition took about 1 hr. The chloroform solution turned pale yellow and no precipitate was formed. The solution was stirred for 30 minutes and the temperature was allowed to rise to −30°. Trimethylamine (25.6 g., 0.44 mole), was then slowly added under vigorous stirring. A rapid reaction took place with formation of a white precipitate. The mixture was allowed to warm slowly to room temperature and then refluxed gently for 2 hr., using an ice-water condenser. All the volatile materials were removed from the flask under pumping vacuum and collected in a trap maintained at −78°. This transfer was continued for 4 hr. with the flask at room temperature and then for 8 hr. with the flask heating on a steam-bath. Fractionation of the volatile materials was achieved by vacuum transfer through U-traps maintained at −10°, −44° and −78°. At −44°, 4.4 g. (12%) of a white crystalline material was recovered (m.p. 64°, sealed capillary).

Anal. Calcd. for $(CF_3)_6P_3N_3$: C, 13.1; N, 7.6; P, 16.9, F, 62.3. Found: C, 13.4; N, 7.8; P, 16.6; F, 62.2.

The molecular weight was determined tensiometrically.

Calcd. for $P_3N_3(CF_3)_6$: mol. wt., 549. Found: mol. wt., 536, 538.

The second fraction collected at −10° was purified by crystallization from *n*-pentane, followed by vacuum sublimation (9.1 g., 25%, m.p. 109°, sealed capillary).

Anal. Calcd. for $(CF_3)_8P_4N_4$: C, 13.1; N, 7.6; P, 16.9; F, 62.3. Found: C, 12.9; N, 7.6; P, 16.6; F, 62.5.

The molecular weight was determined tensiometrically.

Calcd. for $(CF_3)_8P_4N_4$: mol. wt., 732. Found: mol. wt., 716.

The solid residue remaining in the flask after the vacuum transfer was extracted with water to remove the trimethylamine hydrochloride. The white solid material (19.4 g., 53%, m.p. 95–100°) that remained was found to be insoluble in common organic solvents.

Anal. Calcd. for $[(CF_3)_2PN]_n$: C, 13.1; N, 7.6; P, 16.9; F, 62.3. Found: C, 13.1; N, 7.9; P, 16.9; F, 62.3.

Reaction Between Bis-(trifluoromethyl)-dichlorophosphinic Amide, $(CF_3)_2P(Cl)_2NH_2$, and Anhydrous Hydrochloric Acid.—A solution containing 18.5 g. (0.1 mole) of $(CF_3)_2PNH_2$ in 100 ml. of chloroform was cooled to −40° and treated with 7.1 g. (0.1 mole) of chlorine with stirring. The addition was completed in 30 minutes. No precipitate was formed and the solution turned pale yellow. The stirring was continued for about 30 minutes and the temperature was allowed to rise to −30°.

Table I

Infrared Absorptions of Bis-(perfluoroalkyl) Phosphonitriles

$[(CF_3)_2PN]_3$[a]	$[(CF_3)_2PN]_4$[a]	$[(CF_3)_2PN]_n$[b]	$[(C_3F_7)_2PN]_3$[b]
1300[c] s	1412[c] m	1430–1335[c] v.s.	1328[c] s
1205 v.s.	1216 v.s.		1234 v.s.
1166 m	1194 s	1190 s	1120 s
1138 s		1170 s	926 m
		1152 s	868 m
771 m	771 m	900 m	750 m
		775 m	675 m
		682 m	

[a] Spectra obtained in gas phase. [b] Spectra obtained in the solid phase. [c] —P=N— stretching vibration.

A slow stream of anhydrous HCl was then introduced in the flask. An almost immediate reaction occurred with formation of a white precipitate. The addition of HCl was continued for 12 hr., during which time the temperature was maintained at −30° and then for 6 hr. at room temperature. The flask was connected to a vacuum system and all the volatile material was transferred under pumping vacuum to a trap kept at −78°. The residue, after recrystallization from a water–ethanol solution, was identified as NH_4Cl (5.0 g., 93%).

Anal. Calcd. for NH_4Cl: Cl, 66.26; Found: Cl, 66.15.

By fractional distillation of the volatile materials, a liquid boiling at 44–45° (86 mm.) was obtained (24.2 g., 88%).

Analysis of the $(CF_3)_2PCl_3$ was performed by hydrolysis with an excess of 10% NaOH solution. One-half of the trifluoromethyl groups were hydrolyzed as trifluoromethane[13] according to the equation

$$(CF_3)_2PCl_3 + 5NaOH \longrightarrow CF_3H + 3NaCl + CF_3P(O)(ONa)_2 \quad (4)$$

The chlorine was determined by titration of the resulting solution with 0.1 *N* $Hg(NO_3)_2$ standard solution.

Anal. Calcd. for $(CF_3)_2PCl_3$: CF_3 (one-half) 25.45; Cl, 38.7. Found: CF_3, 25.2; Cl, 38.4.

The trifluoromethane recovered was identified by infrared spectroscopy and molecular weight determination (vapor density).

Calcd. for CF_3H: mol. wt., 70. Found: mol. wt., 70.

The molecular weight of $(CF_3)_2PCl_3$ was determined tensiometrically.

Calcd. for $(CF_3)_2PCl_3$: Mol. wt., 275. Found: Mol. wt., 272.

Bis-(heptafluoropropyl)-phosphonitriles, $[(C_3F_7)_2PN]_3$.—A solution containing 44.5 g. (0.1 mole) of $(C_3F_7)_2PNH_2$ in 100 ml. of chloroform was cooled at −30° and under vigorous stirring was treated with 7.1 g. (0.1 mole) of chlorine. The addition took place in about 30 minutes. No precipitate was formed. The solution was stirred for an additional 30 minutes at the same temperature and then combined with 13.0 g. (0.22 mole) of trimethylamine. This resulted in the formation of a white precipitate. After the addition was completed, the solution was allowed to warm to room temperature and was then refluxed for 2 hr. The chloroform was removed under reduced pressure (20 mm.) and the white solid material remaining was extracted with ligroin (65–70°) in a Soxhlet apparatus. Crystallization from hot ligroin solution yielded a white crystalline material (31 g., 70%, m.p. 85°).

Anal. Calcd. for $(C_3F_7)_6P_3N_3$: C, 18.85; N, 3.65; P, 8.1; F, 69.4. Found: C, 19.05; N, 3.8; P, 8.1; F, 69.25.

The molecular weight was determined ebullioscopically in CCl_4.

Calcd. for $(C_3F_7)_6P_3N_3$: mol. wt., 1149. Found: mol. wt., 1139.

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The mother liquor was evaporated to dryness. Upon removal of the residual $[(C_3F_7)_2PN]_3$ by vacuum sublimation, a brown oily material was obtained which was dissolved in boiling benzene. The mixture was cooled to room temperature and a colorless oil was recovered by decantation of the benzene solution. The remaining benzene was removed under vacuum. An extremely viscous colorless oil was obtained whose nature has not yet been established. Infrared spectroscopy of this material strongly suggests the presence of P-N and C-F bonds.

Infrared Spectral Analysis.—The infrared spectra of $[(CF_3)_2PN]_3$ and $[(CF_3)_2PN]_4$ were recorded in the gas phase. The infrared spectra of polymeric $[(CF_3)_2PN]_n$ and $[(C_3F_7)_2PN]_3$ were obtained from thin films prepared by melting the compounds between two sodium chloride plates. The data are shown in Table I.

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[CONTRIBUTION FROM THE OHIO STATE UNIVERSITY RESEARCH FOUNDATION, COLUMBUS 10, OHIO]

A New Class of Stable Phosphonitrilic Acid Esters. Polyfluoroalkyl Phosphonitrilates[1,2]

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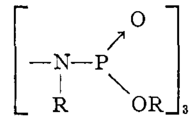
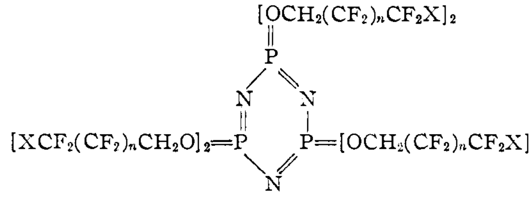
A series of tri- and tetrameric polyfluoroalkyl phosphonitrilates (I and II) has been synthesized. These novel compounds possess remarkable chemical and thermal stability; however, prolonged heating of trimeric bis-(1,1-di-H-heptafluorobutyl)-phosphonitrilate gave ring enlargement to the corresponding tetramer. Most of the compounds of type I and II can be fully chlorinated to hydrogen-free polychloro-polyfluoroalkyl phosphonitrilates.

Esters of the so-called phosphonitrilic acids, $[-N{=}P(OR)_2]_n$ ($n = 3, 4$) can be obtained by complete exchange of the chlorine functions in the cyclic tri- and tetrameric phosphonitrilic chloride by alkoxy- or aryloxy groups. In contrast to the esters of the isomeric trimeta-phosphinic acid[5]

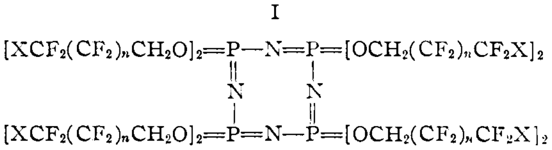


the phosphonitrilic acid esters have never been positively identified and characterized despite the fact that considerable work has been done on this subject.[6] This can be explained by the thermal instability of the phosphonitrilic acid esters. The alkyl phosphonitrilates seem to be especially sensitive compounds which decompose on heating in the range of 100°.[5,7]

In connection with a research program on cyclic phosphorus-nitrogen compounds, a series of new tri- and tetrameric polyfluoroalkylphosphonitrilates (I, II) has been prepared. Their phosphonitrilate structure was elucidated by infrared spectroscopy. The infrared spectra are in agreement with the phosphonitrilate formulas I and II, since strong absorptions are present at 1231 cm.$^{-1}$, indicative for the retention of the aromatic —P=N— ring system. Normally, the —P=N— ring vibration in phosphonitrilic derivatives has been found at 1218 cm.$^{-1}$, but it can be expected that the cumulation of negative fluorine atoms causes a shift to higher frequencies. These esters are accessible in excellent yields by reaction of the cyclic phosphonitrilic chlorides (III) with excess of sodium polyfluoroalkoxides. In contrast to all known phosphonitrilic acid esters, the polyfluoroalkyl phosphonitrilates of the general formulas I and II are thermally very stable, that is, they can be distilled, even at atmospheric pressure, without any decomposition. These compounds are so inert that some of them were purified by distillation in the presence of metallic sodium.



I



II

n = 1, 3, 5, 7, 9
X = F or H
n = 0, 2 only in cases where X = F

While all reported cyclic phosphonitrilic compounds undergo thermal cleavage at approximately 300° to give highly crosslinked polymeric materials, the polyfluoroalkyl phosphonitrilates of type I and II are stable even above this temperature, probably

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(2) This article represents part of a paper delivered by R. Rätz at the Gordon Research Conference on Inorganic Chemistry, New Hampton, N. H., August 1960; parts of the content of this paper are the subject of U. S. Patents 2,876,247 and 2,876,248 (R. F. W. Rätz and C. J. Grundmann to Olin Mathieson Chemical Corporation).

(3) Olin Mathieson Chemical Corporation, New Haven, Connecticut.

(4) To whom inquiries should be directed.

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