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.

Acknowledgments.—This investigation was supported by the Bureau of Naval Weapons, Department of the Navy, through the Foundational Research Program. It is a pleasure to acknowledge the helpful discussions of Dr. C. P. Haber and Dr. P. J. Slota, Jr. The elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

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

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

BY RUDI RÄTZ,[3,4] HANSJUERGEN SCHROEDER,[3] HENRI ULRICH, EHRENFRIED KOBER[3] AND CHRISTOPH GRUNDMANN

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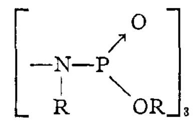
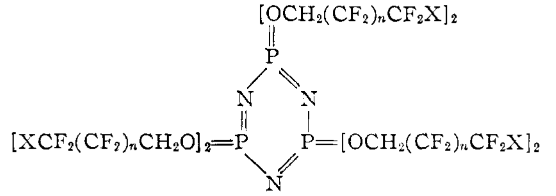
A series of tri- and tetrameric polyfluoroalkyl phosphonitrilates (I and II) has been synthesized. These novel compounds possess remarkable chemical and thermal stability; however, prolonged heating of trimeric bis-(1,1-di-H-heptafluorobutyl)-phosphonitrilate gave ring enlargement to the corresponding 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]

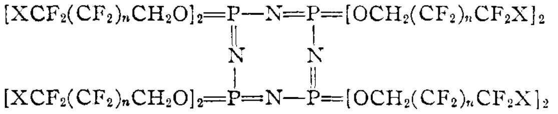


the phosphonitrilic acid esters have never been positively identified and characterized despite the fact that considerable work has been done on this subject.[6] This can be explained by the thermal instability of the phosphonitrilic acid esters. The alkyl phosphonitrilates seem to be especially sensitive 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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[1] This article is based on work performed in 1957 under Project 116-B of The Ohio State University Research Foundation sponsored by the Olin Mathieson Chemical Corporation, New York, N. Y.

[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.

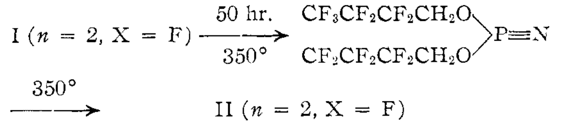
[5] R. Rätz and M. Hess, *Ber.*, **84**, 889 (1951).

[6] L. F. Audrieth, R. Steinmann and A. D. F. Toy, *Chem. Revs.*, **32**, 129 (1943).

[7] Only recently, boiling points of some alkylphosphonitrilates have been reported; B. W. Fitzsimmons and R. A. Shaw, *Chem. and Ind.* (*London*), 109 (1961).

owing to the strong electronegative character of the fluoro atoms of the alkyl group. The fluoroalkoxy substitution stabilizes the whole quasiaromatic —P=N ring moiety to such an extent that formation of polymeric —P=N— chains has not been observed. In addition, these compounds are remarkably resistant to oxidation. The usual analytical method of combustion in a stream of oxygen over copper oxide sometimes does not result in complete oxidation. Neither refluxing with concentrated nitric acid nor refluxing with aqueous base attacks these esters at any measurable rate. However, hydrolysis is effected by refluxing with ethanolic alkali hydroxides.

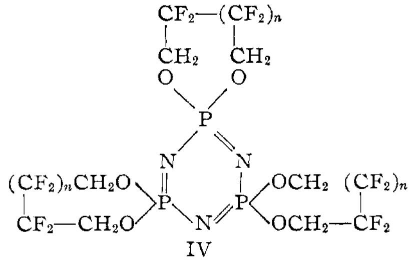
A novel ring enlargement was observed on prolonged heating of trimeric bis-1,1-di-H-heptafluorobutyl phosphonitrilate (I, $n = 2$, X = F). Pure I ($n = 2$, X = F), m.p. 17-18°, prepared from pure trimeric III, which was absolutely free of tetrameric III, was refluxed at 340° for 50 hr. to give, upon slow cooling, the tetrameric oligomer (II, $n = 2$, X = F), m.p. 107°, in a 50% conversion. The identification was accomplished by infrared spectrum, analysis, molecular weight determination and mixed melting point with an authentic sample of II ($n = 2$, X = F). Such a —P=N— ring enlargement might be possible by depolymerization of the trimeric I ($n = 2$, X = F) to smaller units and repolymerization to the tetramer



$$\text{I}\ (n = 2, \text{X} = \text{F}) \xrightarrow[350^\circ]{50\ \text{hr.}} \begin{matrix} CF_3CF_2CF_2CH_2O \\ CF_3CF_2CF_2CH_2O \end{matrix} \!\!> P{\equiv}N \xrightarrow{350^\circ} \text{II}\ (n = 2, \text{X} = \text{F})$$

However, this ring enlargement can also be explained by assuming an equilibrium of the trimer with undetectable amounts of long chains, the latter acting as intermediates in the formation of the tetramer.

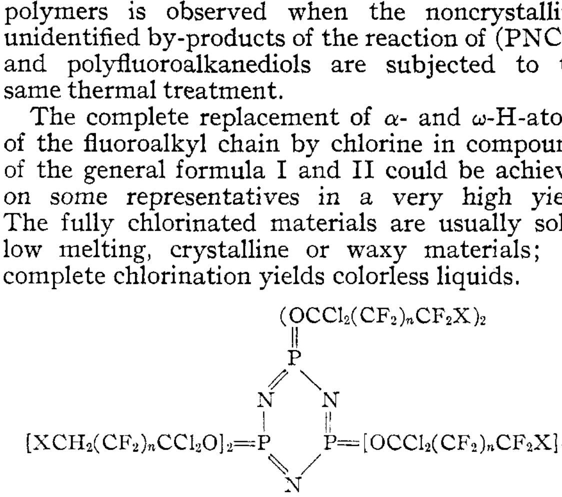
Reaction of trimeric III and sodium- or triethylamine salts of bifunctional fluoroalcohols, such as 1,4-tetrafluorobutanediol and 1,5-hexafluoropentanediol, in refluxing toluene forms a mixture of semi-solid materials. From these mixtures polyfluoroalkylene-phosphonitrilates of the tentative formula IV could be isolated. Compounds of



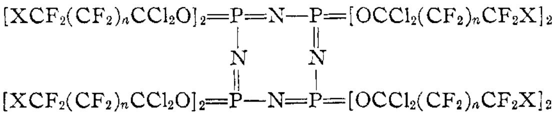
IV

type IV are formed by reaction of each PCl_2 group with one molecule of the diol. Analysis, infrared spectrum and molecular weight determination confirm the assigned "spiro" structure IV. The synthesized representatives of formula IV are as inert chemically as compounds I and II but exhibit considerable decreased thermal stability. Heating IV ($n = 1$ or 2) at temperatures above 300° for a very short period yields brittle polymers which are insoluble in water and all common organic solvents. Formation of similar highly crosslinked polymers is observed when the noncrystalline, unidentified by-products of the reaction of $(PNCl_2)_3$ and polyfluoroalkanediols are subjected to the same thermal treatment.

The complete replacement of α- and ω-H-atoms of the fluoroalkyl chain by chlorine in compounds of the general formula I and II could be achieved on some representatives in a very high yield. The fully chlorinated materials are usually solid, low melting, crystalline or waxy materials; incomplete chlorination yields colorless liquids.



V



VI

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

Such polychloro-polyfluoroalkyl phosphonitrilates of structures V and VI are interesting in many respects. They have the same high chemical and thermal resistance as compounds of type I and II, being incombustible in a Bunsen flame. Compound VI ($n = 9$, X = Cl) has a calculated molecular weight of 5.2 × 10^3 but even yet is distillable at 0.1 mm. It is believed that conventional distillation of such a high molecular weight compound has not been reported before.

Experimental[8]

Starting Materials.—The monofunctional polyfluoroalcohols are commercial products. The tetrafluorobutanediol(1,4) and the hexafluoropentanediol(1,5) were prepared by $Li(AlH_4)$ reduction of diethyl tetrafluorosuccinate and diethylhexafluoroglutarate, respectively, according to known procedures.[9] Tri- and tetrameric phosphonitrilic chloride (III) was prepared according to Schenck and Römer.[10]

Preparation of Tri- and Tetrameric Bis-polyfluoroalkyl Phosphonitrilates.—The sodium-polyfluoroalkoxides were obtained by dissolving the required amount of sodium hydride portionwise in a solution of a 50–80% excess of the appropriate fluoroalcohol in diethyl ether. After complete solution was effected, the ether was removed by distillation and substituted by an equal volume of toluene. The fluoroalkoxide was suspended in the solvent by stirring and gentle heating. After cooling to room temperature, the solution of III in toluene was added dropwise, with stirring, over a period of 30 min. After the exothermic reaction had ceased, the mixture was refluxed for 4 hr. After cooling the reaction mixture to room temperature, the formed sodium chloride was collected on a Buchner funnel. This procedure proved to be effective even in those cases where the oily reaction product was insoluble in toluene at room

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[8] All melting and boiling points are uncorrected. Microanalyses were carried out by the Galbraith Microanalytical Laboratories, Knoxville, Tenn.; molecular weight determinations were by Huffman Microanalytical Laboratories, Wheatridge, Col., and Dr. Carl Tiedcke, Laboratory of Microchemistry, Teaneck, N. J.

[9] E. T. McBee, W. F. Marzluff and O. R. Pierce, *J. Am. Chem. Soc.*, **74**, 444 (1952).

[10] R. Schenck and G. Römer, *Ber.*, **57B**, 1343 (1924).

TABLE I

PROPERTIES OF TRIMERIC POLYFLUOROALKYL PHOSPHONITRILATES

Compound	Yield, %	M.p., °C.; b.p., °C. (mm.)	Recrystallized from	Bruttoformula	Analyses, % Calcd. C	H	F	N	P	Found C	H	F	N	P
Trimeric bis-1,1-di-H-trifluoroethyl phosphonitrilate I, *n* = 0; X = F	99	48; 115–116 (3)	Petroleum ether	$C_{12}H_{12}F_{18}N_3O_6P_3$	19.76	1.66	46.90	5.76	12.75	19.79	2.00	46.06	5.64	12.72
Trimeric bis-1,1-di-H-pentafluoropropyl phosphonitrilate[a] I, *n* = 1; X = F	86.4	16–18; 136.5 (6)	....	$C_{18}H_{12}F_{30}N_3O_6P_3$[c]	21.00	1.17	55.39	4.08	9.03	20.96	1.55	54.23	4.25	9.10
Trimeric bis-1,1-di-H-heptafluorobutyl phosphonitrilate[b] I, *n* = 2; X = F	84	154 (3)	....	$C_{24}H_{12}F_{42}N_3O_6P_3$	21.68	0.91	60.03	3.16	6.99	21.10	1.22	59.62	3.18	6.79
Trimeric bis-1,1,7-tri-H-dodecafluoroheptyl phosphonitrilate I, *n* = 5; X = H	99	33–36; 258–260 (2)	Carbon tetrachloride	$C_{42}H_{18}F_{72}N_3P_3O_6$					4.33					4.47
Trimeric bis-1,1,11-tri-H-eicosafluoroundecanyl phosphonitrilate I, *n* = 9; X = H	80	103–105; 320–324 (2)	Toluene	$C_{66}H_{18}F_{120}N_3P_3O_6$	23.83	0.53		1.27	2.83	23.44	0.77		1.42	3.17
Trimeric 1,1,4,4-tetra-H-tetrafluorotetramethylene phosphonitrilate IV, *n* = 1	22.6	300	Toluene	$C_{12}H_{12}F_{12}N_3O_6P_3$	23.40	1.95	37.04	6.83	15.11	23.67	1.89	36.90	6.74	15.24
Trimeric 1,1,5,5-tetra-H-hexafluoropentamethylene phosphonitrilate IV, *n* = 2	10.3	242–244	Toluene	$C_{15}H_{12}F_{18}N_3O_6P_3$[d]	23.55	1.57	44.7	5.50	12.13	24.33	1.64	43.1	6.03	12.24

[a] $n^{28}D$ 1.3365. [b] $n^{25}D$ 1.3309. [c] Molecular weight by ebullioscopic method in benzene, 835; calcd. 1029. [d] Molecular weight by Rast method, 631; calcd. 615.

TABLE II

PROPERTIES OF TETRAMERIC POLYFLUOROALKYL PHOSPHONITRILATES

Compound	Yield, %	M.p., °C.; b.p., °C. (mm.)	Recrystallized from	Bruttoformula	Analyses, % Calcd. C	H	F	N	P	Found C	H	F	N	P
Tetrameric bis-1,1-di-H-trifluoroethyl phosphonitrilate; II, *n* = 0; X = F	89	65; 139–140 (3)	Petroleum ether	$C_{16}H_{16}F_{24}N_4O_8P_4$	19.76	1.66	46.90	5.76	12.75	19.82	2.13	45.79	5.79	12.75
Tetrameric bis-1,1-di-H-pentafluoropropyl phosphonitrilate[a]; II, *n* = 1; X = F	89	142–144 (3)	....	$C_{24}H_{16}F_{40}O_8P_4$[c]	21.00	1.17	55.39	4.08	9.03	20.97	1.50	55.37	4.14	9.07
Tetrameric bis-1,1-di-H-heptafluorobutyl phosphonitrilate; II, *n* = 2; X = F	81	107; 169.5–171.5 (3)	Petroleum ether	$C_{32}H_{16}F_{56}N_4O_8P_4$	21.68	0.91	60.03	3.16	6.99	21.88	0.93	59.99	3.21	7.12
Tetrameric bis-1,1,7-tri-H-dodecafluoroheptyl phosphonitrilate[b]; II, *n* = 5; X = H	93	265 (1)	....	$C_{56}F_{24}F_{96}N_4O_8P_4$	23.78	0.85	64.48	1.98	4.38	22.15	1.33	64.06	2.59	4.29
Tetrameric bis-1,1,11-tri-H-eicosafluoroundecanyl phosphonitrilate; II, *n* = 9; X = H	90	102–105; 312–320 (0.1)	Toluene	$C_{88}H_{24}F_{160}N_4O_8P_4$	23.83	0.53		1.27	2.83	22.41	0.86		1.52	2.83

[a] $n^{27}D$ 1.3530. [b] $n^{27}D$ 1.3441. [c] Molecular weight by ebullioscopic method: 1190; calcd. 1372.

temperature. However, it was then necessary to remove the adhering oil from the sodium chloride by washing with a small amount of ether. The toluene was removed by distillation and the entire remaining residue was then fractionally vacuum distilled to obtain the pure polyfluoroalkyl phosphonitrilates of type I and II listed in Table I and Table II.

As a typical example, the amounts of the reactants for the preparation of trimeric bis-1,1-di-*H*-heptafluorobutylphosphonitrilate (I, *n* = 2, X = F) are: 200 g. of heptafluorobutanol dissolved in 320 ml. of ether, 14.4 g. of sodium hydride, 320 ml. of toluene added after removal of the ether and 34.8 g. of trimeric III dissolved in 110 ml. of toluene.

Trimeric 1,1,4,4-Tetra-*H*-tetrafluorotetramethylene Phosphonitrilate (IV, *n* = 1).—A solution of tetrafluorobutanediol-1,4 (32.5 g. = 0.2 mole, 100% excess) in 100 ml. of ether was placed in a 250 ml. three-neck flask equipped with stirrer, condenser and dropping funnel. Then 4.8 g. of sodium hydride (0.2 mole) was added portionwise. The mixture was refluxed for 24 hr. to dissolve the NaH completely. After removing the ether by distillation, the remaining solid was suspended in 200 ml. of dry toluene. A solution of 9 g. of trimeric III (0.026 mole) in 50 ml. of toluene was added dropwise, with stirring, over a period of 30 min. Refluxing and stirring was continued for 18 hr. Then, after appropriate cooling, the cold mixture was filtered by using a Buchner funnel. By extracting the collected solid material with hot toluene, 3.6 g. of IV (*n* = 1, Table I) was obtained.

By evaporating the toluene filtrate in a moderate vacuum and by treating the obtained residue several times with 50 ml. portions of water at 40°, unreacted fluorobutanediol was dissolved and 12 g. of a noncrystalline, semi-plastic product, presumably a mixture of polyfluoroalkylene phosphonitrilates of higher molecular weight, was obtained. This product was still ether-soluble but could not be subjected to vacuum distillation without polymerization which gave a brittle, insoluble polymer.

Trimeric 1,1,5,5-tetra-*H*-hexafluoropentamethylene Phosphonitrilate, (IV, *n* = 2).—The preparation of this compound was carried out in a somewhat modified manner to that applied for IV (*n* = 1).

To a solution of 21.2 g. of hexafluoropentanediol-1,5 (0.1 mole) in 270 ml. of dry toluene, 40 g. of dry triethylamine was added. Then a solution of 10 g. of trimeric III (0.029 mole) in 70 ml. of toluene was added dropwise, with stirring, over a period of 30 min. The reaction mixture was refluxed for 18 hr. Filtration of the hot solution gave 22.0 g. of triethylamine hydrochloride (calcd. 23.7 g.). After removing the toluene from the filtrate by distillation, an amount of 17 g. of a highly viscous, brown oil remained from which, after addition of 75 ml. of ether, white crystals (2.25 g.) separated after several days (IV, *n* = 2, Table I). The ether was removed by distillation from the ethereal filtrate to give semi-plastic, thermally unstable material.

Tetrameric Bis-1,1-di-*H*-heptafluorobutyl Phosphonitrilate (II, *n* = 2, X = F) by Prolonged Heating of the Trimer (I, *n* = 2, X = F).—Trimeric III used for the preparation of I (*n* = 2, X = F) was twice distilled over a Vigreux column in order to ensure complete separation from traces of contaminating tetrameric III. The trimeric III, thus obtained, had a boiling point of 127.5° (13 mm.) and melted at 114°. The ester I (*n* = 2, X = F) obtained from this double-distilled trimeric III showed the same physical properties as a sample of I (*n* = 2, X = F) prepared from single-distilled trimeric III, m.p. 113°.

An amount of 10 g. of the above mentioned I (*n* = 2, X = F) was placed into a 50 ml. two-necked round bottom flask equipped with gas inlet tube and air condenser. The flask was heated by means of a metal bath at 340° for 50 hr. while a slow stream of nitrogen was passed over the surface of the refluxing material. After subsequent cooling, an amount of 5 g. of a waxy product separated which, after two recrystallizations from ligroin (b.p. 90–97°), showed a melting point of 107° and proved to be identical with II (*n* = 2, X = F). A mixed melting point with an authentic sample showed no depression.

Anal. Calcd. for $(C_8H_4F_{14}NPO_2)_x$: C, 21.68; H, 0.91; F, 60.03; N, 3.16; P, 6.99. Found: C, 21.96, 21.95; H, 1.37, 1.34; F, 59.62, 59.61; N, 3.34, 3.38; P, 6.92, 7.04.

Table III

Tri- and Tetrameric Polychloro-polyfluoroalkyl Phosphonitrilates

Compound	Yield, %	M.p., °C. b.p., °C. (mm.)	Recrystallized from	Bruttoformula	Analyses, % Calcd. C	Calcd. Cl	Calcd. F	Calcd. N	Calcd. P	Found C	Found Cl	Found F	Found N	Found P
Trimeric bis-1,1-dichloro-2,2,3,3,3-pentafluoropropyl phosphonitrilate V, *n* = 1; X = F	100	147–148; 176 (5)	Benzene	$C_{18}Cl_{12}F_{30}N_3O_6P_3$		29.60		2.91	6.45		29.49		2.86	5.88
Trimeric bis-1,1-dichloro-2,2,3,3,4,4,4-heptafluorobutyl phosphonitrilate V, *n* = 2; X = F	99	94; 194–197 (4)	Ethyl acetate or petroleum ether	$C_{24}C_{12}F_{42}N_3O_6P_3$	16.54	24.41	45.79	2.41	5.33	16.56	22.52	45.25	2.46	5.24
Tetrameric bis-1,1-dichloro-heptafluorobutyl phosphonitrilate V, *n* = 2; X = F	55	129–132; 234 (3)	Petroleum ether	$C_{32}Cl_{16}F_{56}N_4O_8P_4$	16.54	24.41		2.41	5.33	16.63	22.68		2.39	5.47
Tetrameric bis-1,1,11-trichloroeicosafluoroundecanyl phosphonitrilate V, *n* = 9; X = Cl	99	145–149	Ligroin	$C_{88}Cl_{24}F_{160}N_4O_8P_4$		16.40			2.36		16.09			2.44

TABLE IV

INFRARED ABSORPTION MAXIMA, WAVE LENGTH IN MICRONS

I, $n = 2$, X = F	II, $n = 2$, X = F	Thermal rearrangement product
14.86 m	14.88 v.w.	14.88 w
13.65 m	13.60 w	13.61 w
13.15 s	13.25 m	13.26 m
12.97 m	12.60 w	12.64 w
12.17 s		
11.33 s	11.32 w	11.33 w
10.83 vs	10.74 m	10.74 m
10.32 vs	10 33m	10.34 m
9.83 vs	9.83 s	9.84 s
9.18 vs	9.17 vs	9.18 vs
8.87 vs	8.84 vs	8.86 vs
8.45 vs	8.45 vs	8.46 vs
8.13 vs	8.13 vs	8.14 vs
7.70 m	7.67 m	7.68 m
7.37 vs	7.45 vs	7.44 vs
7.09 m	7.08 m	7.08 m
6.84 m		
5.05 vw		
4.04 vw		
3.44 vw		
3.35 w	3.35 vw	3.34 vw

Calcd. for $C_{32}H_{16}F_{56}N_4P_4O_8$: mol. wt. determination (Rast) 1772; found: 1638, 1612.

α,α-Dichloro-polyfluoroalkyl- and α,α,ω-Trichloro-polyfluoroalkyl Phosphonitrilates. *Trimeric Bis-1,1-dichloro-pentafluoropropyl Phosphonitrilate (V, $n = 1$, $X = F$)*.—Eight g. of I ($n = 1$, X = F) was dissolved in 50 ml. of carbon tetrachloride and the solution exposed to ultraviolet light, while a stream of dry chlorine gas was passed in for 48 hr. After removal of the solvent by distillation in a moderate vacuum, a waxy residue was obtained which was redissolved in ether for subsequent extractions with sodium bicarbonate solution and water. After drying the ethereal solution with sodium sulfate and removing the solvent by distillation, the obtained residue was subjected to vacuum distillation to give compound V ($n = 1$, X = F, Table III).

Trimeric Bis-1,1-dichloro-heptafluorobutyl Phosphonitrilate (V, $n = 2$, X = F) was obtained by similar chlorination of 120 g. of I ($n = 2$, X = F) in 1200 ml. of carbon tetrachloride with the exception that the flow of the chlorine gas was extended to 96 hr.

Tetrameric Bis-1,1-dichloro-heptafluorobutyl Phosphonitrilate (VI, $n = 2$, X = F) was obtained by passing a slow stream of chlorine into 23.2 g. of molten II ($n = 2$, X = F) at 90° for 3 days. After this time, chlorination was continued for 3 additional days at room temperature. Resinous impurities were removed by adding petroleum ether (b.p. 90–97°) to the reaction product. The remaining crystalline VI ($n = 2$, X = F) amounted to 12 g.

Tetrameric Bis-1,1,11-trichloro-eicosa-fluoroundecanyl Phosphonitrilate (VI, $n = 9$, X = Cl).—Ten g. of compound II ($n = 9$, X = H) was melted and chlorine passed into the melt at 170° oil-bath temperature. After 4 days, complete exchange of all hydrogen by chlorine atoms had been achieved.

Stability Tests on Bis-1,1-di-*H*-polyfluoroalkyl Phosphonitrilates.—A 5 g.-sample of I ($n = 1$, X = F) was heated at 210° and a rapid stream of dry air passed in for 1 hr. The refractive index of I ($n = 1$, X = F) did not change at all after this treatment. (b) A sample of II ($n = 2$, X = F; 0.403 g.) was refluxed in 10 ml. of 68% nitric acid for 1 hr. After subsequent cooling, an amount of 0.38 g. of unchanged colorless II ($n = 2$, X = F) was recovered. After two recrystallizations from petroleum ether (b.p. 90–97°) the melting point was found to be 107° (compared with 107° before the refluxing). Treatment of the nitric acid mother liquor with ammonium-molybdate reagent gave no indication for the presence of monophosphate ions. (c) A sample of II ($n = 2$, X = F; 0.2849 g.) was refluxed with 15 ml. of 30% aqueous sodium hydroxide for 1 hr. An amount of 0.260 g. of a slightly brown crystalline material was recovered which became colorless after washing with 5 ml. of water. After two recrystallizations from petroleum ether, the unchanged product melted at 107°.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, RESEARCH AND DEVELOPMENT CENTER, ARMSTRONG CORK COMPANY LANCASTER, PA.]

The Reaction of Neutral Esters of Trivalent Phosphorus Acids with Inorganic Acid Chlorides. III. The Reaction of Trialkyl Phosphites with Thionyl Chloride[1]

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The reaction between thionyl chloride and a trialkyl phosphite gives a mixture of a dialkyl phosphorochloridate, a trialkyl phosphorothionate, a trialkyl phosphate, an alkyl chloride and sulfur dioxide in relative amounts dependent upon reaction conditions. The reaction is vigorous even at −60° and intermediate adducts are not observed. Sulfur monoxide is speculated as a primary reaction intermediate to account for the results obtained. Sulfur dichloride reacts with triethyl phosphite to give diethyl phosphorochloridate and triethyl phosphorothionate as major non-volatile products. Sulfur dioxide converts trialkyl phosphites into trialkyl phosphorothionate and trialkyl phosphate at about 100°.

Introduction

The application of phosphorus compounds as pneumatogens to provide a gas for expanding resinous compositions into foamed plastics prompted some studies on the reaction of neutral esters of trivalent phosphorus acids with a variety of inorganic acid chlorides. Thionyl and sulfuryl chlorides were reported, but without adequate evidence, to give moderately stable 1:2 adducts with trialkyl phosphites.[2] Such adducts with phosphites of lower alkyl homologs, which were claimed to decompose into alkyl halides only at temperatures above 100°, would have applications for expanding plastics into cellular or spongeous products. Unfortunately for the anticipated application as pneumatogens, our attempts to prepare

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[1] Presented before the Division of Inorganic Chemistry at the September 1959 Meeting of the American Chemical Society, Atlantic City, N. J.

[2] A. Bell, U. S. Patent 2,508,364 (1950).