ene (XIII) (2.1 g, mp 160–162°; 2.5 g, mp 157–160°). The rest (11.5 g) of the water-insoluble products were combined and chromatographed on acid-washed alumina (462 g). From fractions 22–32, pure XIII (2.3 g), mp 157–160°, was obtained, and fractions 39–59 gave XIV (3.1 g), mp 152–155°. Fractions 60–62 crystallized overnight and afforded, after recrystallization from ethanol, 2,2-diamino-4,4-diphenoxy-6,6-diphenylcyclotriphosphazatriene (XII), mp 150–152°, which did not depress the melting point upon admixture with a sample prepared by the other route, described in the following section. Fractions 13–20 crystallized 4 months later, and 2-amino-2,4,4-triphenoxy-6,6-diphenylcyclotriphosphazatriene (XI) (1.25 g), mp 79–83°, was collected. A sample was dissolved in ether, and the solution was diluted with an equal volume of hexane and left standing in an open flask with seeding to give 0.7 g of prisms, mp 93–95°. An analytical sample of XI, obtained after one more recrystallization, melted at 93.5–95.5°.

TABLE VI

Fraction	Solvent	Total vol, ml	Eluate, g	Remarks
1–9	Benzene	1320	Trace	
10–11	1:4 ether–benzene	230	0.08	Light oil
12–21	1:4 ether–benzene	1230	2.06	XI
22	1:4 ether–benzene	70	0.20	XIII
23–32	2:3 ether–benzene	1200	3.03	XIII
33–38	3:2 ether–benzene	590	0.16	oil
39–49	3:2 ether–benzene	1100	1.64	XIV
50–54	4:1 ether–benzene	500	0.79	XIV
55–59	Ether	730	0.69	XIV
60–62	Methanol	200	1.06	XII
63–64	Methanol	400	Trace	

The total yields of the aminophenoxy compounds based on the starting 2,2,4,4-tetrachloro-6,6-diphenylcyclotriphosphazatriene are summarized as follows: XI, 4.6% (1.25 g, 0.00214 mole); XII, 4.5% (1.06 g, 0.00209 mole); XIII, 33.2% (7.8 g, 0.0154 mole); XIV, 39.4% (9.3 g, 0.0183 mole).

2,2-Diamino-4,4-diphenoxy-6,6-diphenylcyclotriphosphazatriene (XII).—2,2-Diamino-4,4-dichloro-6,6-diphenylcyclotriphosphazatriene (5.0 g, 0.0128 mole; mp 161–165°) was treated with sodium phenoxide (0.050 mole) in boiling acetone (200 ml) for 24 hr, and XII, mp 145–151°, was obtained in 71% yield (4.6 g, 0.091 mole). Recrystallization from ethanol gave a pure sample (3.8 g), mp 150–152°.

2,2,4,4-Tetraphenoxy-6,6-diphenylcyclotriphosphazatriene.—2,2,4,4-Tetrachloro-6,6-diphenylcyclotriphosphazatriene (5.00 g, 0.0116 mole) was treated with sodium phenoxide (0.051 mole) in boiling acetone (280 ml) for 24 hr, and crude 2,2,4,4-tetraphenoxy-6,6-diphenylcyclotriphosphazatriene, mp 79.5–81.5°, was obtained in 79% yield (6.09 g, 0.0082 mole). Recrystallization from ethanol gave a sample, mp 97–98°.

Anal. Calcd for $P_3N_3(C_6H_5)_2(OC_6H_5)_4$: C, 65.36; H, 4.57; N, 6.35. Found: C, 65.16; H, 4.72; N, 6.61.

Check of Absence of Isomerization during Phenoxylation.—A solution of *cis*-2,4-dichloro-2,4,6,6-tetraphenoxycyclotriphosphazatriene (II) (5.00 g, 0.00865 mole; mp 74–76°) and sodium phenoxide (0.0030 mole) in acetone (200 ml) was stirred for 24 hr at room temperature and then evaporated. To the residue ether and water were added; the ether layer was separated and the aqueous layer extracted once with ether. The combined ether solution was dried ($CaCl_2$) and evaporated leaving an oil (6.97 g), which contained acetone. The oil was dissolved in ether (80 ml), and the solution was left standing with liquid ammonia (*ca.* 100 ml) in an autoclave for 96 hr. The resulting mixture was filtered, the filtrate was evaporated, and the remaining oil (5.97 g) was chromatographed on acid-washed alumina (150 g). Aminopentaphenoxycyclotriphosphazatriene (III), mp 65–67°, and then *cis*-2,4-diamino-2,4,6,6-tetraphenoxycyclotriphosphazatriene (VI), mp 117–119°, were eluted, but no *trans*-2,4-diamino-2,4,6,6-tetraphenoxycyclotriphosphazatriene (V) was found in the 38 chromatographic fractions. On the basis of the totals of the corresponding chromatographic fractions, the yields of III and VI were 1.61 g (0.00261 mole, 30%) and 2.97 g (0.00551 mole, 64%), respectively.

CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT,
U. S. NAVAL PROPELLANT PLANT, INDIAN HEAD, MARYLAND

Synthesis and Characterization of Some Perfluorophenylphosphine Derivatives[1,2]

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Bis(pentafluorophenyl)chlorophosphine and pentafluorophenyldichlorophosphine are prepared in good yields from pentafluorophenylmagnesium bromide and phosphorus trichloride. The reactions of the halophosphines with the Lewis bases water, ammonia, dimethylamine, and 2-methylaziridine produced substituted phosphines. Oxidative chlorination of bis(pentafluorophenyl)phosphinamide followed by dehydrohalogenation gave perfluorophenylphosphonitriles. The infrared and pertinent proton magnetic resonance spectra of these compounds are discussed.

Introduction

A synthetic approach similar to that used by Wall and co-workers[3] was employed in the preparation of bis(pentafluorophenyl)chlorophosphine (I) and pentafluorophenyldichlorophosphine (II) from pentafluorophenylmagnesium bromide[4] and phosphorus trichloride in stoichiometric amounts.

$$2C_6F_5MgBr + PCl_3 \longrightarrow \underset{\text{I}}{(C_6F_5)_2PCl} + 2Mg(Br)Cl$$

$$C_6F_5MgBr + PCl_3 \longrightarrow \underset{\text{II}}{C_6F_5PCl_2} + Mg(Br)Cl$$

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(1) This work was supported by the Foundational Research Program of the Bureau of Naval Weapons.

(2) (a) Presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964; (b) presented in part at the 3rd International Fluorine Chemistry Symposium, Munich, Germany, Aug 1965.

(3) L. A. Wall, R. E. Donadio, and W. T. Pummer, *J. Am. Chem. Soc.*, **82**, 4846 (1960).

(4) E. Nield, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 166 (1959).

Halophosphines undergo many of the usual addition reactions which are characteristic of trivalent phosphorus compounds; also, being essentially acid halides, they undergo many replacement reactions involving the highly reactive halogen atoms.[5] Because of the highly reactive phosphorus–chlorine bond of these chlorophosphines, it was possible to prepare the other compounds herein described.

Experimental Section

Technical grade pentafluorobenzene was obtained from Imperial Smelting Corp., Ltd., and was brominated as described by Nield, Stephens, and Tatlow.[4] A constant-boiling fraction of bromopentafluorobenzene (bp 134–135°) was used in the preparation of pentafluorophenylmagnesium bromide. All melting and boiling points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc.

Bis(pentafluorophenyl)chlorophosphine (I).—An ether solution of pentafluorophenylmagnesium bromide (300 mmoles) was added dropwise to an ether solution of phosphorus trichloride (20.58 g, 150 mmoles) under a nitrogen blanket with cooling and stirring. After addition was completed, the solution was filtered with the exclusion of air, and the ether was evaporated under reduced pressure. A dark brown oil remained which was fractionally distilled using a platinum spinning-band column to give bis(pentafluorophenyl)chlorophosphine (39.42 g, 66%), bp 111–112° (1.3 mm). *Anal.* Calcd for $C_{12}ClF_{10}P$: C, 36.0; P, 7.7; F, 47.4; Cl, 8.9. Found: C, 35.6; P, 7.4; F, 47.4; Cl, 8.5.

Pentafluorophenyldichlorophosphine (II).—An ether solution of pentafluorophenylmagnesium bromide (300 mmoles) was added to an ether solution of phosphorus trichloride (41.22 g, 300 mmoles) under nitrogen with cooling and stirring. By techniques described in the preparation of I a dark brown oil was isolated. Fractional distillation with a platinum spinning-band column gave pentafluorophenyldichlorophosphine (44.56 g, 55%), bp 81–82° (9 mm). *Anal.* Calcd for $C_6Cl_2F_5P$: C, 26.8; P, 11.5; F, 35.3; Cl, 26.4. Found: C, 25.8; P, 11.1; F, 33.3; Cl, 24.2.

Bis(pentafluorophenyl)phosphinous Acid (III).—Bis(pentafluorophenyl)chlorophosphine (3.99 g, 10 mmoles) was added under nitrogen to 20 ml of distilled water with stirring and cooling. A white solid formed which was broken up to facilitate stirring. The mixture was stirred for 1 hr and filtered under nitrogen through a glass frit. The solid product was divided into two portions, one handled in air and the other under nitrogen. Both portions were recrystallized several times from *n*-hexane to give pure bis(pentafluorophenyl)phosphinous acid (3.12 g, 82%). Potentiometric titration gave $\mathrm{p}K_a = 4.38$ in 50 vol % ethanol solution. Each fraction melted at 97–98°, and a mixture melting point showed no depression. *Anal.* Calcd for $C_{12}HF_{10}OP$: C, 37.7; H, 0.3; P, 8.1; F, 49.7. Found: C, 37.4; H, 0.4; P, 8.1; F, 49.5.

Pentafluorophenylphosphonous acid (IV).—A dioxane solution of pentafluorophenyldichlorophosphine (6.41 g, 24 mmoles) was slowly added under nitrogen to 50 ml of distilled water with cooling and stirring. After addition was completed, the clear, colorless solution was stripped of solvent under reduced pressure, leaving a white crystalline mass. Recrystallization several times from benzene gave pure pentafluorophenylphosphonous acid (1.16 g, 21%), mp 81–83°, a monobasic acid with $\mathrm{p}K_a =$ 4.40 (determined by potentiometric titration in 50 vol % ethanol solution). *Anal.* Calcd for $C_6H_2F_5O_2P$: C, 31.1; H, 0.9; P, 13.6; F, 40.9. Found: C, 31.3; H, 1.0; P, 13.3; F, 40.7.

Bis(pentafluorophenyl)phosphinamide (V).—Anhydrous ammonia gas was bubbled through a cooled benzene solution of bis(pentafluorophenyl)chlorophosphine (3.49 g, 8.7 mmoles) for 1 hr. The formation of ammonium chloride was almost immediate. The solution was filtered through a glass frit, and the solvent was evaporated under reduced pressure. The remaining milky oil crystallized on standing. The solid material was sublimed at 40–50° (0.05 mm) to give pure bis(pentafluorophenyl)phosphinamide (2.35 g, 71%), mp 63–65°. *Anal.* Calcd for $C_{12}H_2F_{10}NP$: C, 37.8; H, 0.5; P, 8.1; F, 49.8; N, 3.9. Found: C, 37.7; H, 0.4; P, 8.2; F, 49.8; N, 3.9.

Bis(dimethylaminotetrafluorophenyl)-N,N-dimethylphosphinamide (VI).—An excess of anhydrous dimethylamine was bubbled through an ether solution of bis(pentafluorophenyl)chlorophosphine (4.57 g, 11 mmoles) with cooling. Dimethylamine hydrochloride was formed almost immediately. The resulting solution was filtered through a sintered-glass funnel, and the solvent was stripped off leaving an amber oil (4.45 g, 95.5%). Pure bis(dimethylaminotetrafluorophenyl)-N,N-dimethylphosphinamide (mp 70.5–71.0°) was obtained by alternately freezing and thawing a concentrated pentane solution of the product and finally recrystallizing from methanol. *Anal.* Calcd for $C_{18}H_{18}F_8N_3P$: C, 47.1; H, 3.9; N, 9.1; P, 6.7; F, 33.1. Found: C, 46.9; H, 4.0; N, 9.0; P, 6.7; F, 33.0.

Pentafluorophenylbis(N,N-dimethyl)phosphonodiamide (VII).—An excess of anhydrous dimethylamine was bubbled through an ether solution of pentafluorophenyldichlorophosphine (23.19 g, 86 mmoles) with cooling under nitrogen. The dimethylamine hydrochloride was removed by filtration, and the ether was evaporated under reduced pressure, leaving an amber oil (20.5 g, 81.5%). Distillation over a short path gave pure pentafluorophenylbis(N,N-dimethyl)phosphonodiamide, bp 54° (0.1 mm). *Anal.* Calcd for $C_{10}H_{12}F_5N_2P$: C, 42.0; H, 4.2; P, 10.8; F, 33.2; N, 9.8. Found: C, 41.8; H, 4.3; P, 11.0; F, 32.9; N, 9.5.

Bis(pentafluorophenyl)[1-(2-methyl)aziridinyl]phosphine (VIII).—A solution containing 16.00 g (40 mmoles) of bis(pentafluorophenyl)chlorophosphine in 300 ml of dry ether under nitrogen was cooled to 0° and with stirring was treated dropwise with a 50-ml ether solution containing 4.04 g (40 mmoles) of triethylamine and 2.28 g (40 mmoles) of 2-methylaziridine. The solution became turbid with the first drop of the aziridine–triethylamine solution, and triethylamine hydrochloride precipitated on further addition. After the addition had been completed, the solution was stirred for 1 hr. The triethylamine hydrochloride (4.75 g, 88%) was removed by filtration, and the solvent was evaporated under reduced pressure, leaving 15.12 g (90% yield) of an amber oil. Vacuum distillation of this oil on a steam bath gave pure bis(pentafluorophenyl)[1-(2-methyl)aziridinyl]phosphine, bp 85° (0.05 mm). *Anal.* Calcd for $C_{15}H_6F_{10}NP$: C, 42.8; H, 1.4; P, 7.4; F, 45.1; N, 3.3. Found: C, 42.4; H, 1.6; P, 7.2; F, 45.2; N, 3.3.

Bis(pentafluorophenyl)dichlorophosphinamide (IX).—Generated *in situ* by the oxidative chlorination of V.

Bis(pentafluorophenyl)phosphonitrile (X).—A solution containing 2.44 g (6.4 mmoles) of bis(pentafluorophenyl)phosphinamide in 50 ml of dry methylene chloride was cooled to −25° and with stirring was treated with 0.46 g (6.4 mmoles) of dried chlorine. The solution turned pale yellow, but no precipitate formed. The solution was stirred at −25° for 30 min and was further cooled to −80°. Triethylamine (1.30 g, 12.8 mmoles) was slowly added to the reaction mixture with stirring. A reaction readily occurred with formation of a white precipitate, and the mixture was allowed to warm to room temperature. The solvent was evaporated under vacuum, and the solid material was washed with 20 ml of water and filtered on a fritted-glass funnel. Evaporation of the water from the filtrate and drying in a desiccator left 1.47 g (83.5% yield) of the triethylamine hydrochloride.

Fractional crystallization of the residue (2.32 g) from benzene gave 0.79 g (34.5% of residue) of the white crystalline trimer mp 307–309°. Evaporation of the mother liquor under vacuum left 1.53 g (65.5% of residue) of an amorphous solid, mp 79–90°. *Anal.* Calcd for $C_{12}F_{10}NP$: C, 38.0; P, 8.2; F, 50.1; N, 3.7; mol wt of $C_{36}F_{30}P_3N_3$, 1137. Found for crystalline material: C, 37.8; P, 8.0; F, 49.8; N, 3.5; mol wt, 1177 (determined by

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[5] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, pp 42–57.

the Rast camphor method; 0.22 *m* concentration). Found for amorphous material: C, 38.1; P, 8.2; F, 50.0; N, 3.9.

Results and Discussion

Bis(pentafluorophenyl)phosphinous Acid (III).—The hydrolysis of secondary monohalophosphines rarely gives the expected phosphinous acids; rather, disproportionation occurs to give phosphonic acids and the corresponding phosphines as in the case of diphenylchlorophosphine[6]

$$2(C_6H_5)_2PCl + 2H_2O \longrightarrow (C_6H_5)_2PH + (C_6H_5)_2PO_2H + 2HCl$$

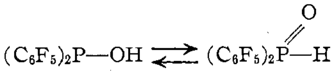
In marked contrast to this, the hydrolytic disproportionation of bis(trifluoromethyl)iodophosphine gives fluoroform and trifluoromethylphosphonous acid[7]

$$(CF_3)_2PI + 2H_2O \longrightarrow CF_3H + CF_3PO_2H_2 + HI$$

However, bis(pentafluorophenyl)chlorophosphine fails to show this tendency to disproportionate and gives only bis(pentafluorophenyl)phosphinous acid (III).

$$\underset{}{(C_6F_5)_2PCl + H_2O \longrightarrow} \underset{\text{III}}{(C_6F_5)_2POH} + HCl$$

The infrared spectrum of III did not show bands which could be assigned to P—OH, P—H, or P=O vibrations and was therefore of little help in the characterization of this acid. However, the proton magnetic resonance spectrum of III in deuteriochloroform consists of one line at 4.00 ppm and another broad band at 13.3 ppm downfield from tetramethylsilane. The line at 4.00 ppm is due to a phosphorus-bonded hydrogen, and the band at 13.3 ppm is due to a combination of the split phosphorus-bonded hydrogen and the hydroxyl group. From the ratio of the integrated resonance intensities III exists in the two tautomeric forms



$$\underset{\text{IIIa}}{(C_6F_5)_2P{-}OH} \rightleftarrows \underset{\text{IIIb}}{(C_6F_5)_2\overset{O}{\overset{\|}{P}}{-}H}$$

In deuterated dimethyl sulfoxide the proton magnetic resonance spectrum of this acid is quite different. It consists of only one band at 16.0 ppm due to a hydroxyl group, thus indicating that the equilibrium is totally shifted to IIIa by this more polar solvent.

Pentafluorophenylphosphonous Acid (IV).—A second monobasic acid, pentafluorophenylphosphonous acid (IV), is similarly obtained by the hydrolysis of pentafluorophenyldichlorophosphine

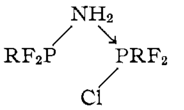
$$C_6F_5PCl_2 + 2H_2O \longrightarrow \underset{\text{IV}}{C_6F_5PO_2H_2} + 2HCl$$

It has been pointed out by Bailey and Fox[8] that the infrared spectra of phosphonous acids are unsuitable for the assignment of P–H and P–OH absorptions because of greatly broadened bands in the 2–6-μ region owing to hydrogen bonding. In the sodium salt, however, this broad absorption is absent. A sharp P–H band is observed at 2401 cm^{-1}, indicating the structure of this salt is $C_6F_5PH(:O)(ONa)$ rather than $C_6F_5P(OH)(ONa)$. This evidence is further supported by the proton magnetic resonance spectrum of the free acid in deuteriochloroform. The spectrum consists of a line at 13.2 ppm due to the hydroxyl group and a doublet with one line at 13.0 ppm and one line at 2.43 ppm due to a spin–spin splitting of the phosphorus-bonded hydrogen. The coupling constant of 636 cps is of the same order of magnitude as that found by Reuben and co-workers[9] for phenylphosphonous acid.

Bis(pentafluorophenyl)phosphinamide (V).—Many compounds have been obtained from the reaction of amines with phosphine halides,[10] but they are frequently not those predicted by the simple elimination of hydrogen halide. The first compound of the phosphinamide type was bis(trifluoromethyl)phosphinous amide, $(CF_3)_2PNH_2$, reported by Harris.[11] In this study, it has been found that the reaction between bis(pentafluorophenyl)chlorophosphine and ammonia proceeds smoothly to bis(pentafluorophenyl)phosphinamide (V) and ammonium chloride.

$$(C_6F_5)_2PCl + 2NH_3 \longrightarrow \underset{\text{V}}{(C_6F_5)_2PNH_2} + NH_4Cl$$

That neither $(CF_3)_2PNH_2$ nor V reacts with another molecule of the respective phosphine halides in the absence of a suitable proton acceptor[12] excludes the possibility of the formation of the intermediate (A). This can be readily explained by the fact that the π-electron density on the nitrogen atom is greatly diminished by pπ–dπ bonding between the filled p orbital of the nitrogen and the vacant d orbitals of the phosphorus, thus removing the donor characteristics of the nitrogen atom and reinforcing those of the phosphorus atom. This is supported by Ewart and co-workers,[13] who found that methyl iodide adducts of a variety of phosphonodiamides did not deviate from a 1:1 formulation. Also, their proton magnetic resonance spectrum of the 1:1 methyl iodide adduct formed by phenylbis(N,N-diethyl)phosphonodiamides indicates that the methyl group is attached directly to the phosphorus. In the cases of the formation of $(CF_3)_2PNH_2$ and $(C_6F_5)_2PNH_2$, the possibility of the electronegative CF_3 and C_6F_5 groups affecting the pπ–dπ bonding must not be excluded.



A

Bis(dimethylaminotetrafluorophenyl)-N,N-dimethylphosphinamide (VI).—Bubbling an excess of dimethylamine through an ether solution of I cooled to ice bath temperature did not give the expected phosphinamide, $(C_6F_5)_2PN(CH_3)_2$. Rather, a secondary reaction oc-

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[6] C. Dörken, *Ber.*, **21**, 1505 (1888).

[7] H. T. Emeléus, R. N. Haszeldine, and R. C. Paul, *J. Chem. Soc.*, 563 (1955).

[8] W. J. Bailey and R. B. Fox, *J. Org. Chem.*, **29**, 1013 (1964).

[9] J. Reuben, D. Samuel, and B. L. Silver, *J. Am. Chem. Soc.*, **85**, 3093 (1963).

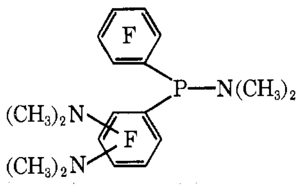
[10] See ref 5, pp 278–324.

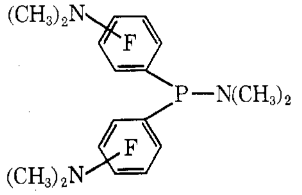
[11] G. S. Harris, *J. Chem. Soc.*, 512 (1958).

[12] A. B. Burg and J. Heners, *J. Am. Chem. Soc.*, **87**, 3092 (1965).

[13] G. Ewart, D. S. Payne, A. L. Porte, and, in part, A. P. Lane, *J. Chem. Soc.*, 3984 (1962).

curred whereby two dimethylamino groups were introduced into the perfluorophenyl ring system and gave either compound VIa or VIb.


VIa

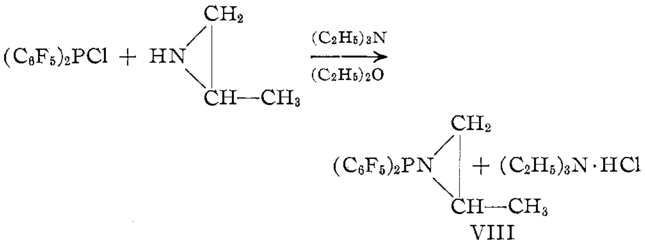

VIb

Mass spectrometric fragmentation studies showed the presence of a dimethylaminotetrafluorophenyl fragment, $C_6F_4N(CH_3)_2^+$ (mass peak 192), and a tetrafluorophenyl fragment, $C_6F_4^+$ (mass peak 148). There was no evidence of a pentafluorophenyl fragment, $C_6F_5^+$ (mass peak 167), or a bis(dimethylamino)trifluorophenyl fragment, $C_6F_3[N(CH_3)_2]_2^+$ (mass peak 217). Therefore, it appears that a dimethylamino group substituted for a fluorine atom on each ring to give VIb. The position of the dimethylamino group on the fluoroaromatic ring was not established.

Pentafluorophenylbis(N,N-dimethyl)phosphonodiamide (VII).—The reaction between dimethylamine and II proceeds smoothly, the bulk of the amine hydrochloride being precipitated almost immediately, to pentafluorophenylbis(N,N-dimethyl)phosphonodiamide (VII). This compound forms a 1:1 mercuric iodide complex similar to its phenyl analog prepared by Ewart and co-workers;[13] however, the complex slowly decomposes in light and readily decomposes in solution to release droplets of metallic mercury.

$$C_6F_5PCl_2 + 4HN(CH_3)_2 \longrightarrow \underset{\text{VII}}{C_6F_5P[N(CH_3)_2]_2} + 2HCl\cdot HN(CH_3)_2$$

Bis(pentafluorophenyl)[1-(2-methyl)aziridinyl]phosphine (VIII).—The reaction of 2-methylaziridine with I resulted in the amide containing the unique cyclic imine structure (VIII). It was necessary to adjust the reaction conditions so as to avoid the simultaneous opening of the imine ring. This was achieved by maintaining a low reaction temperature and the use of triethylamine as the acid acceptor.


VIII

The imine ring of VIII apparently is easily opened even under ambient conditions. The infrared spectrum of the compound that had been allowed to stand open to the air exhibited two new absorption bands at 3436 and 1727 cm^{-1} which were not present in the spectrum of the pure compound. Also, extensive decomposition of the crude material occurred during the vacuum distillation at steam bath temperature, giving a large amount of resins. Further studies of substituted aziridine derivatives of bis(pentafluorophenyl)chlorophosphine are in progress.

Bis(pentafluorophenyl)phosphonitrile (X).—Oxidative chlorination of bis(pentafluorophenyl)phosphinamide, V, followed by dehydrohalogenation of the chlorinated derivative (IX) with a tertiary amine produced a high-melting crystalline trimer and a low-melting amorphous fraction. Analyses of both fractions indicate the general formula to be $[(C_6F_5)_2PN]_n$ (X)

$$\underset{\text{V}}{(C_6F_5)_2PNH_2} + Cl_2 \xrightarrow{CH_2Cl_2} \underset{\text{IX}}{[(C_6F_5)_2P(Cl_2)NH_2]}$$

$$\underset{\text{IX}}{[(C_6F_5)_2P(Cl_2)NH_2]} + 2(C_2H_5)_3N \xrightarrow{CH_2Cl_2} \underset{\text{X}}{[(C_6F_5)_2PN]_n} + 2(C_2H_5)_3N\cdot HCl$$

The molecular weight of the trimer was determined by the Rast camphor method because of its extremely low solubility in organic solvents.

Infrared Spectra.[14]—A comparison of the infrared spectra of seven of the perfluorophenylphosphine derivatives with that of deuterated pentafluorobenzene, possessing C_{2v} symmetry,[15] revealed that the pentafluorophenyl vibrations were virtually unperturbed by the presence of the phosphorus groups.

The chlorophosphines demonstrated characteristic P–Cl absorptions at 509 and 422 cm^{-1} in the case of I and at 498 and 415 cm^{-1} in the case of II.

The spectra of the phosphinous and phosphonous acids did not show bands which could be assigned to P—OH, P—H, or P=O vibrations. However, in the sodium salt of the phosphonous acid, as was previously mentioned, a sharp band was found at 2401 cm^{-1}, which was assigned to a P–H stretching mode.

The infrared spectrum of bis(pentafluorophenyl)phosphinamide exhibits two sharp maxima at 3482 and 3395 cm^{-1} for N–H stretching vibrations and one NH_2 deformation band at 1565 cm^{-1}.

The only bands found that were characteristic for bis(dimethylaminotetrafluorophenyl)-N,N-dimethylphosphinamide are the C–H stretching bands in the 2930–2810-cm^{-1} region and one C–H deformation band at 1381 cm^{-1}. For pentafluorophenylbis(N,N-dimethyl)phosphonodiamide there are C–H stretching bands in the 2965–2790 cm^{-1} region and one C–H deformation band at 1366 cm^{-1}. No characteristic P–N band was found in these compounds. This is no surprise, for the P–N vibrations have been found over a wide range in phosphonitrilic compounds.

Although no assignments were attempted for vibrational mode characteristics of C_6F_5–P, all of the compounds exhibited strong absorption bands at 1491–1460, 982–951, and 762–757 cm^{-1}. Daasch and Smith[16] reported strong bands at 1400 and 1000 cm^{-1} for similar type compounds.

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[14] Infrared spectra obtained from a Perkin-Elmer 421 spectrophotometer in the frequency range of 4000–200 cm^{-1}.

[15] D. Steele and D. Wiffen, *Trans. Faraday Soc.*, **55**, 369 (1959).

[16] L. S. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

TABLE I

CALCULATED "INDUCTIVE" SUBSTITUENT CONSTANTS AND RELATED P=N STRETCHING VIBRATIONS OF $X_6P_3N_3$

X	σ_I	$\nu_{P=N}$, cm^{-1}
CH_3	−0.05	1180
C_6H_5	0.10	1190
C_6F_5	0.23[a]	1200
CF_3	0.30	1205

[a] Determined from plot of σ_I *vs.* $\nu_{P=N}$.

The infrared absorption spectra of the bis(pentafluorophenyl)phosphonitriles display a strong band at 1200 cm^{-1} in the case of the trimer and broad medium bands in the same region for the amorphous material. It is interesting to note the comparison of the "inductive" substituent constants[17] on the P_3N_3 nucleus with their respective P=N absorptions.[18] These data are listed in Table I.

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Synergistic Effect of Tri-*n*-octylamine on the Solvent Extraction of Americium by Thenoyltrifluoroacetone[1]

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The synergistic effect of tri-*n*-octylamine (R_3N) on the solvent extraction of americium by thenoyltrifluoroacetone (HT) is shown to arise from organic phase reactions $AmT_3 + R_3NHCl = AmT_3R_3NHCl$, $AmT_3 + R_3NHT = AmT_3R_3NHT$, and $AmT_3 + R_3NHClHT = AmT_3R_3NHClHT$, where T^- represents the enolate ion of HT. It was ascertained that the formation constants for each of these reactions are the same. The formation constants were measured in benzene as $\log K_s = 5.03 \pm 0.20$. The formation constant for the addition reaction $AmT_3 + HT = AmT_3HT$ was measured as $\log K_{Am,HT} = 0.75 \pm 0.05$. Reasons are presented which lead to the conclusion that in the products of synergism each of the amine species is attached directly to the americium. The synergistic effect was studied for values of pH which were varied from 1.1 to 5.7.

Introduction

The synergistic effect of tri-*n*-octylamine (TNOA) on the solvent extraction of thorium by thenoyltrifluoroacetone (TTA) has already been studied.[2] Throughout this paper R_3N represents TNOA and T^- the enolate ion of TTA. Only R_3NHCl was found to cause a synergistic effect. Since TTA coordinately saturates the thorium it is difficult to understand how the bond is formed between the ThT_4 and the R_3NHCl. Americium(III) was selected for this work in order to study the nature of the synergistic effect exerted by TNOA on an element which is possibly coordinately unsaturated by TTA. The object of this investigation was, therefore, to determine which species of the amine can cause the synergistic effect, the values of the equilibrium constants involved, and the nature of the species formed.

Experimental Section

The source and purification of TTA and TNOA have previously been described.[3] Americium (Am^{241}) was obtained from Oak Ridge National Laboratory. It was found to be free of γ-emitting contaminants in the energy range of 0 to 1.5 Mev. All other chemicals used were of reagent grade. The stock lithium chloride solutions were filtered prior to use.

In all experiments, the aqueous phase consisted of 2 *M* LiCl except for one series which was 0.01 *M* in chloride. The organic diluent was benzene. The distribution experiments were performed with equal volumes. The activity of the americium in the aqueous phase prior to contact was $\sim 5 \times 10^4$ counts min^{-1} ml^{-1}.

A titration technique was adopted in which, for a given experiment, the TTA and TNOA concentrations were maintained constant in the organic phase and the pH of the aqueous phase was increased by the addition of alkali. The experiments were conducted in a stoppered cylindrical glass vessel which accommodated a glass electrode, a buret with an elongated tip, and a glass "dip" tube employed for taking aliquots from the aqueous (lower) phase. Aliquots from the organic phase were taken directly through a hole in the stopper. The phases were mixed by employing a magnetic stirrer. After equilibration ($\sim$10 min) the solutions were allowed to separate, and 2-ml aliquots taken from both phases were γ counted in a "well-type" scintillation counter. Then another addition of alkali was made. The volume of the organic phase was kept equal to the aqueous by the addition of a corresponding amount of the original organic solution. Equilibrium was ascertained by contacting for longer periods of time and by performing a reverse titration.

The free TTA concentration was kept constant by accounting for the amount consumed in reaction with the amine. The constants involved and the method employed have been described.[2] Although the form of the bound TTA was changed when varying the hydrogen ion concentration, the over-all excess needed remained relatively constant. The amount of

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(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

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