panied by decomposition, and additional products could not be isolated.

Reaction of octyne-1 with bis(2-cyanoethyl)phosphine. A mixture of 28.0 g. (0.2 mole) of the phosphine, 22.0 g. (0.2 mole) of octyne-1, 1.5 g. (0.01 mole) of α,α'-azobisisobutyronitrile, and 25 ml. of dry benzene was heated under nitrogen with stirring to 68°. A mild exotherm occurred, and the mixture became homogeneous. The solution was heated at 80–85° for 45 min. and distilled to obtain 3.0 g. (11%) of unchanged starting phosphine and 15.0 g. (30%) of bis(2-cyanoethyl)-1-octenyl-phosphine, b.p. 176–190° (0.6 mm.). A center cut, b.p. 187–190° (0.6 mm.), n_D^{25} 1.5000, was analyzed.

Anal. Calcd. for $C_{14}H_{23}PN_2$: C, 67.17; H, 9.26, N, 11.20; P, 12.37. Found: C, 66.97; 9.35; N, 11.20; P, 12.58.

The infrared spectrum was identical to that of the heptenyl analog.

Reaction of heptyne-1 with 2-cyanoethylphosphine. A solution of 8.7 g. (0.1 mole) of the phosphine, 9.6 g. (0.1 mole) of heptyne-1, and 0.75 g. (0.005 mole) of α,α'-azobisisobutyronitrile was heated under nitrogen at 80–85° for 2 hr. The orange reaction mixture was distilled to obtain 4.1 g. (47%) of unchanged starting phosphine and 3.6 g. (26%) of 2-cyanoethylbis(1-heptenyl)phosphine, b.p. 130–145° (0.2 mm.). Redistillation of the latter provided an analytical sample b.p. 140° (0.25 mm.), n_D^{25} 1.4930.

Anal. Calcd. for $C_{17}H_{30}NP$: C, 73.07; H, 10.82; P, 11.09. Found: C, 73.34; H, 11.10; P, 11.19.

The infrared spectrum showed the presence of a double bond and the absence of a P—H bond.

Further distillation of the reaction mixture resulted in decomposition.

Reaction of acetylene with bis(2-cyanoethyl)phosphine. Into a 300-ml. stainless steel autoclave were placed 50.0 g. (0.36 mole) of the phosphine 5.9 g. (0.07 mole) of α,α'-azobisisobutyronitrile, and 75 ml. of tetrahydrofuran. The autoclave was closed, evacuated, and charged to 4.4 atm. with dry nitrogen. The autoclave was then rocked while acetylene was added to a pressure of 13.6 atm. The autoclave was heated with rocking at 80° for 4 hr. The reaction mixture was stripped of solvent to obtain a yellow oil. The infrared spectrum indicated only a trace of olefinic unsaturation. An attempt made to distil one half of the product was unsuccessful because of extensive decomposition. Also unsuccessful were attempts to induce crystallization of the product or to prepare crystalline derivatives by oxidation with hydrogen peroxide or quaternization with methyl iodide.

Acknowledgment. The authors are indebted to D. J. Wilson and M. Sabia for assistance with the pressure experiments and to R. L. Webb for the x-radiation experiments. The authors also wish to express their sincere appreciation to Mrs. E. C. Grim, Dr. J. A. Kuck, and associates for microanalyses, to N. Colthup for infrared spectra, and to Dr. J. E. Lancaster for NMR spectra.

STAMFORD, CONN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

Further Studies of the Synthesis of *N*-Substituted Aminodiphenylphosphines

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The chlorodiphenylphosphination reaction has been extended to nine additional aliphatic and aromatic amines and resulted in the preparation of 2-pyridylaminodiphenylphosphine, *N*-methylbutylaminodiphenylphosphine, morpholinodiphenylphosphine, ethyleniminodiphenylphosphine, hexamethyleniminodiphenylphosphine, and *P*-3(3-azabicyclo[3.2.2]-nonyl)diphenylphosphine. Under other than anhydrous conditions, the chlorodiphenylphosphination of dibenzylamine and 1,1,3,3-tetramethylbutylamine yielded dibenzylaminodiphenylphosphine oxide dihydrate and 1,1,3,3-tetramethylbutylaminodiphenylphosphine oxide hydrate. The aminodiphenylphosphines were converted to the corresponding oxides and/or sulfides.

In a recent communication[1] we reported the synthesis of some *N*-substituted aminodiphenylphosphines by the direct chlorodiphenylphosphination of aliphatic and aromatic amines. Further work in our laboratory has resulted in the synthesis of several new compounds which extends significantly the range of these chlorophosphination reactions. The additional aminophosphines are 2-pyridylaminodiphenylphosphine, *N*-methylbutylaminodiphenylphosphine, morpholinodiphenylphosphine, ethyleniminodiphenylphosphine, hexamethyleniminodiphenylphosphine, and *p*-3(3-azabicyclo[3.2.2]nonyl)diphenylphosphine.

The *N*-substituted aminodiphenylphosphines derived from chlorophosphination reactions are viscous liquids or crystalline solids which are very reactive toward water, alkylation reagents, and certain metal salts. Some of the syntheses involve reactions that are best conducted under an anhydrous, inert atmosphere. Under other than anhydrous conditions, the chlorodiphenylphosphination of dibenzylamine and 1,1,3,3-tetramethylbutylamine results in the formation of dibenzylaminodiphenylphosphine oxide dihydrate and 1,1,-3,3 - tetramethylbutylaminodiphenylphosphine oxide hydrate.[2]

The aminodiphenylphosphines were converted

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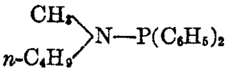
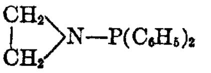
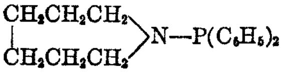
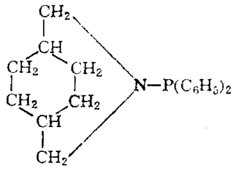
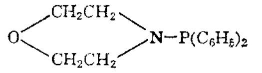
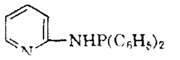
(1) H. H. Sisler and N. L. Smith, *J. Org. Chem.*, **26**, 611 (1961).

(2) The oxide hydrates of these aminophosphines might be considered quasiphosphonium type compounds since their infrared spectra show a phosphonium type structure with principal bands at 1120 cm.$^{-1}$ and in the region 940–820 cm.$^{-1}$ See J. C. Sheldon and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*, **80**, 2117 (1958).

TABLE I

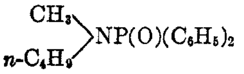
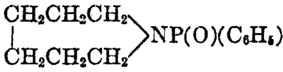
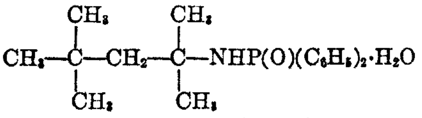
SOME *N*-SUBSTITUTED AMINODIPHENYLPHOSPHINES

Formula	Yield, %	M.P. or B.P.	Calcd., % Found, %			
			C	H	N	P
 $CH_3(n\text{-}C_4H_9)N—P(C_6H_5)_2$	68	118–122[a] (0.06 mm)	75.25 74.81	8.17 8.58	5.16 5.19	11.42 11.44
	26[b]	155–156[a] (0.8 mm)	73.99 73.92	6.21 6.04	6.13 6.11	13.63 13.54
	70	76.5–77.5[c]	76.29 76.12	7.83 7.93	4.94 4.96	10.93 11.06
	34	82–84[b,c]	77.64 77.58	7.82 8.03	4.53 4.55	10.01 9.93
	96 (Crude)	86–87[c]	70.83 70.64	6.69 6.59	5.16 4.99	11.42 11.67
	54	142.0–142.5[c]	73.36 73.16	5.43 5.25	10.06 9.89	11.13 10.95

[a] B.p. [b] The referee has suggested the possibility that the low yield with the diphenylchlorophosphination may have resulted from ring opening and polymerization. [c] M.p.

TABLE II

SOME *N*-SUBSTITUTED AMINODIPHENYLPHOSPHINE OXIDES

Formula	Yield	M.P. or B.P.	Calcd., % Found, %			
			C	H	N	P
$t\text{-}C_4H_9NHP(O)(C_6H_5)_2$	66	136–136.5[a]	70.31 70.45	7.37 7.29		
 $CH_3(n\text{-}C_4H_9)NP(O)(C_6H_5)_2$	87	160–164[b] (0.4 mm)	71.56 71.34	7.06 7.78	4.91 5.19	10.86 11.44
	93	118.5–119.5[a]	72.22 72.06	7.41 7.62		
 $CH_3—C(CH_3)_2—CH_2—C(CH_3)_2—NHP(O)(C_6H_5)_2 \cdot H_2O$	81	257–258[a]	69.14 69.06	8.70 8.38	4.03 4.47	8.92 9.23
$(C_6H_5CH_2)_2NP(O)(C_6H_5)_2 \cdot 2H_2O$	16	141–143[a]	72.04 72.35	6.51 6.85	3.23 3.37	7.15 7.20

[a] M.p. [b] B.p.

to either the corresponding aminodiphenylphosphine oxide or aminodiphenylphosphine sulfide, and in some cases both.

Of the several methods used to obtain tertiary phosphine oxides, the direct oxidation of the tertiary phosphine using oxygen, hydrogen peroxide, and nitric acid[3,4] proved troublesome when applied to the synthesis of aminodiphenylphosphine oxides. Our novel oxidation of aminodiphenylphosphines with activated manganese dioxide proved particularly effective in preparing the aminodiphenylphosphine oxides. The reaction proceeds rapidly, cleanly, and in satisfactory yields in the presence of an inert solvent.

A recent Russian article[5] reports the preparation of aminodiphenylphosphine oxide (amide of diphenylphosphinic acid) by direct amidation of diphenylphosphinyl chloride. This method appears to be generally applicable for the preparation of aminophosphine oxides but its usefulness is limited by the fact that it depends on the availability of

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(3) L. P. Kuhn, J. O. Doole, and C. Wellman, *J. Am. Chem. Soc.*, **82**, 4792 (1960).

(4) K. D. Berlin and G. B. Butler, *Chem. Revs.*, **60**, 243 (1960).

(5) I. N. Zhmurova, L. Voitsckhovskasa, and A. V. Kirsanov, *J. Gen. Chem. U.S.S.R.*, 29, 2052 (1959) (English translation).

TABLE III. SOME N-SUBSTITUTED AMINODIPHENYLPHOSPHINE SULFIDES

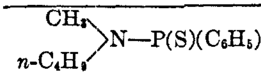
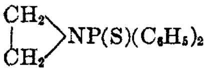
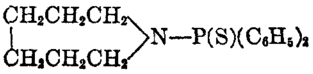
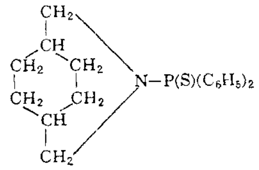
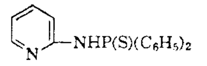
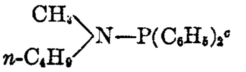
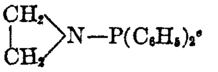
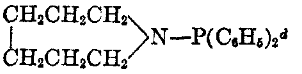
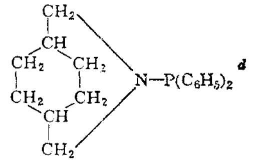
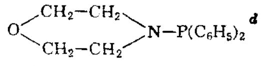
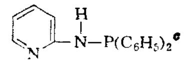
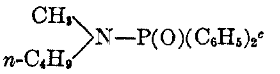
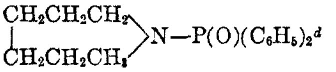
Formula	Yield, %	M.P.	Calcd., % Found, % C	H	S
 $(CH_3)(n\text{-}C_4H_9)N-P(S)(C_6H_5)_2$	73	56–57	67.29 67.14	7.31 7.56	10.57 10.75
 $(CH_2)_2NP(S)(C_6H_5)_2$	57	70.5–71.5	64.85 64.64	5.44 5.38	12.36 12.56
 $(CH_2CH_2CH_2)_2N-P(S)(C_6H_5)_2$	60	90–91	68.54 68.36	7.03 7.11	10.17 10.35
	80	128–129	70.35 70.17	7.08 6.89	9.39 9.40
	74	138.0–140.5	65.78 65.57	4.87 4.93	10.33 10.49

TABLE IV. PRINCIPAL INFRARED BANDS FOR SOME AMINODIPHENYLPHOSPHINES[a,b]

Formula	
 $(CH_3)(n\text{-}C_4H_9)N-P(C_6H_5)_2{}^{c}$	2950s 1440m 1360w 1210w 109m 1000m (doublet) 935w 745s 725w 695s
 $(CH_2)_2N-P(C_6H_5)_2{}^{e}$	3000s 1480s 1440s 1240s 1095s 995w 900s (doublet) 810m 750s 700s
 $(CH_2CH_2CH_2)_2N-P(C_6H_5)_2{}^{d}$	3000s 1440s 1160m 1050s 1000w 900m 855w 750s 700s
	3000s 1440m 1170w 1090m 1040m 995w 910s 830w 740s 695s
	3000s 1435m (doublet) 1360s 1250s 1110s 1070w 1010s 940s 840w 750s 725m 700s
	3400w 3050w 1600s 1480s 1440s 1305m 1150w 1090w 990w 910m 775m 740s 695s

[a] s = strong, m = medium, w = weak. [b] Cm.$^{-1}$ ± 3. [c] Melt on sodium chloride plates. [d] Nujol mulls on sodium chloride plates. [e] Liquid on potassium bromide plates.

TABLE V. PRINCIPAL INFRARED BANDS FOR SOME AMINODIPHENYLPHOSPHINE OXIDES[a,b]

Formula	
$t\text{-}C_4H_9NHP(O)(C_6H_5)_2{}^{c}$	3250m 3000s 1590w 1475m 1440s 1355m (doublet) 1180s 1110s 1065m 1030m 1000m 925w 855w 750s 720w 700s
 $(CH_3)(n\text{-}C_4H_9)N-P(O)(C_6H_5)_2{}^{c}$	2995m 1185s 1120s 1000m 940m 870w 745w 725s 700s
 $(CH_2CH_2CH_2)_2N-P(O)(C_6H_5)_2{}^{d}$	1590w 1440s 1340s 1220m 1185s 1150m 1120s 1030m 1000w 940w 895m 755m 725s 705m
$t\text{-}C_8H_{17}{}^{e}NHP(O)(C_6H_5)_2\cdot H_2O^{d}$	3400w 2995s 1610m 2800–2600 (broad band) 1440m 1360m 1180s 1120s (doublet) 1040m 1000w 750w 725s 700m
$(C_6H_5CH_2)_2N-P(O)\text{-}(C_6H_5)_2\cdot 2H_2O^{d}$	3000w 1600w (2800–2200) 1440m 1190w 1120s 1030m 995w 920w 820w 750m (doublet) 720m 700s

[a] s = strong, m = medium, w = weak. [b] Cm.$^{-1}$ ± 3. [c] Melt on sodium chloride plates. [d] Nujol mulls on sodium chloride plate.

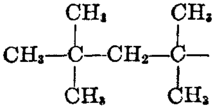
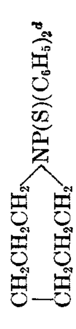
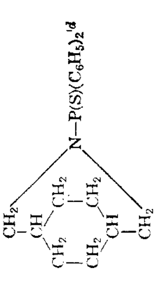
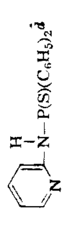
[e]  $CH_3-C(CH_3)_2-CH_2-C(CH_3)_2-$

TABLE VI

PRINCIPAL INFRARED BANDS FOR SOME *N*-SUBSTITUTED AMINODIPHENYLPHOSPHINE SULFIDES[a,b]

Formula									
 $N—P(S)(C_6H_5)_2$[c]	3000s	1580w	1480m	1435s			1110s	1000m 935s	875w 750s 715s 700s
 $NP(S)(C_6H_5)_2$[c]	3000w		1480w	1440s	1250s		1110s 1040w	1000w 935s	820m 750s 720s 690s
 $NP(S)(C_6H_5)_2$[d]	3000s			1440s			1130w 1095w 1030w	1000w 940w 890w 960w	750m 715s 700m
 $N—P(S)(C_6H_5)_2$[d]	2950s			1440s	1370w		1140w 1115s 1080w 1040m	1000w 915s	860w 845w 755s 715s 695s
 $N—P(S)(C_6H_5)_2$[d]	3000s	1600m (doublet)	1495s	1450s	1435m	1300s	1150w 1110s	1000m 940s (doublet)	870w 780m 745m 720s 700s

[a] s = strong, m = medium, w = weak. [b] Cm.$^{-1}$ ± 3. [c] Melt on sodium chloride. [d] Nujol mulls on sodium chloride plates.

disubstituted phosphinyl chlorides. For confirmational purposes, we prepared *t*-butylaminodiphenylphosphine oxide by an extension of the Russian method. Its physical properties were shown to be identical with those of the compound prepared by the direct oxidation of *t*-butylaminodiphenylphosphine.

Unlike the aryl-substituted tertiary phosphine oxides, which possess great thermal and chemical stability,[4,6] our results with the aminodiphenylphosphine oxides indicate a lack of these properties. Some of the aminodiphenylphosphine oxides were isolated with difficulty because of their tendency to form unstable hydrates and their poor crystallizability from most solvents. In some cases the oxide decomposed during attempts to distill it even at reduced pressure.

The *N*-substituted aminodiphenylphosphine sulfides reported herein were prepared by the direct reaction of sulfur[7] with the corresponding aminophosphine. These reactions were ordinarily carried out in ethyl ether, benzene, or carbon disulfide. As the reactions are exothermic, the sulfur was added slowly. Conversion of the aminodiphenylphosphines to aminodiphenylphosphine sulfides raised the melting point in most cases as was noted with the aminodiphenylphosphine oxides.

EXPERIMENTAL[8]

Materials. Diphenylchlorophosphine was obtained from Victor Chemical Co. and used as received. Activated manganese dioxide was obtained from Beacon Chemical Industries, Inc. The sources of the amines used are *N*-methylbutylamine from Union Carbide Chemicals Co.; ethylenimine from Matheson Co., Inc.; hexamethylenimine from Du Pont; 3-azabicyclo[3.2.2]nonane from Eastman Chemical Products, Inc.; morpholine from Union Carbide Chemicals Co.; 2-aminopyridine from Distillation Products Industries; dibenzylamine from Sumner Chemical Co., and 1,1,3,3-tetramethylbutylamine from Rohm and Haas. All the amines in this investigation were used as received.

Procedure for the chlorophosphination reaction. As an example of the procedure used in the direct chlorophosphination of the amines, the preparation of hexamethyleniminodiphenylphosphine is described.

A solution of 22.0 g. (0.10 mole) of diphenylchlorophosphine in 100 ml. of ethyl ether was added dropwise with stirring to a chilled solution of 22.0 g. (0.22 mole) of hexamethylenimine in 150 ml. of dry ethyl ether. The rate of addition was adjusted to keep the temperature between −5° and 0°. Stirring was continued for an additional hour after the addition of the diphenylchlorophosphine was completed. The reaction mixture was filtered and the amine hydrochloride precipitate was washed with small portions of dry ethyl ether. The combined filtrate and washings were stripped of solvent by rotary vacuum evaporation. The residue crystallized on standing, (m.p. 70–72°) and weighed 28.2 g. The product was fractionated, (b.p. 165–171°/0.025 mm), and crystallized on cooling. It crystallized from aqueous

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(6) P. W. Morgan and B. C. Heir, *J. Am. Chem. Soc.*, **74**, 4526 (1960).

(7) J. R. Van Wazer, *Phosphorus and Its Compounds*, Interscience, New York, 1958, Vol. I.

(8) All melting and boiling points are uncorrected. Microanalyses were done by Galbraith Laboratories, Knoxville, Tenn.

acetone as glistening plates, (m.p. 76.5–77.5°) and weighed 19.9 g. (70% yield).

The physical properties, yields, and analytical data for this compound and other aminodiphenylphosphines prepared in this investigation are compiled in Table I. Infrared spectral data for the aminodiphenylphosphines are listed in Table IV.

Procedure for the oxidation of the aminophosphines. Hexamethyleniminodiphenylphosphine, as well as several other aminophosphines prepared, was converted to the corresponding aminophosphine oxides by the reaction of activated manganese dioxide in accordance with the following procedure:

To a stirred solution of 2.8 g. (0.01 mole) of hexamethyleniminodiphenylphosphine in 75 ml. of dry benzene was added 5.2 g. (0.06 mole) of activated manganese dioxide. The mixture was stirred at reflux for 2 hr., cooled, and filtered. The solid was washed with small portions of benzene. The solvent from the combined filtrate and washings was removed by rotary vacuum evaporation and the residue air dried. The product weighed 2.8 g. (93% yield) and melted at 118.0–119.5°. It crystallized from acetone as white granules (m.p. 118.5–119.5°).

The oxidation of *t*-butylaminodiphenylphosphine[1] by the procedure described yielded *t*-butylaminodiphenylphosphine oxide in 66% yield. To confirm the structure the compound was prepared by an alternate method:

A solution of 23.6 g. (0.01 mole) of diphenylphosphinyl chloride in 30 ml. of dry benzene was added gradually over a period of 20 min. to a chilled (5–10°) solution of 18.3 g. (0.25 mole) of *t*-butylamine in 100 ml. of dry benzene. Anhydrous ethyl ether (100 ml.) was added to the solution to precipitate *t*-butylamine hydrochloride. The mixture was filtered and the solids washed twice with ethyl ether. The combined filtrate and washings were stripped of solvent by rotary vacuum evaporation leaving a solid residue. This product was recrystallized twice from an *n*-hexane-benzene mixture to give long thick needles, (m.p. 134–136°) and weighed 10.5 g. (39% yield). It crystallized from hot water in long needles (m.p. 136–137°). The identity of this compound with that prepared by the oxidation of *t*-butylaminodiphenylphosphine was established by physical constants (melting point and mixed melting point and infrared spectra).

Analytical data, yield data, and melting or boiling points for the *N*-substituted aminodiphenylphosphine oxides are summarized in Table II. Infrared spectral data for these compounds are listed in Table V.

Procedure for the formation of aminophosphine sulfides. The *N*-substituted aminodiphenylphosphine sulfides were obtained from corresponding *N*-substituted aminodiphenylphosphines by treatment with sulfur in an inert solvent. The preparation of hexamethyleniminodiphenylphosphine sulfide is used to illustrate the general procedure:

Sulfur (0.3 g., 0.01 g. mole) was added slowly to a stirred solution of 2.8 g. (0.01 mole) of hexamethyleniminodiphenylphosphine in 25 ml. of dry benzene. The mixture was stirred at reflux for 1 hr. The solvent was removed by rotary evaporation and the viscous residue was crystallized from ethanol. It crystallized from acetone in large prisms, (m.p. 90–91°) and weighed 1.9 g. (60% yield).

Physical properties, yields, and analytical data for the aminodiphenylphosphine sulfides prepared are compiled in Table III. Those features of the infrared spectra used in confirming assigned structure are listed in Table VI.

Because of the unusual character of the derivatives of 3-azabicyclo[3.2.2]nonane it should be specifically noted that the infrared spectra of the starting material, the chlorophosphination product, and the corresponding sulfide were carefully compared and correlated. The strong N—H band at 3330 cm.$^{-1}$ in the starting material disappears completely in the chlorophosphination product. This combined with excellent analytical data and a consideration of the mode of synthesis establishes beyond reasonable doubt the structure assigned.

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The Use of Hexafluorophosphoric Acid in the Schiemann Reaction[1]

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The preparation of some fluoroaromatic hydrocarbons *via* decomposition of intermediate diazonium hexafluorophosphates is reported. A comparison is made with the normal Schiemann Reaction which involves decomposition of diazonium tetrafluoroborates. This investigation shows that hexafluorophosphoric acid is a very useful reagent for the conversion of $ArNH_2$ to ArF and in some cases a marked improvement is realized over the use of fluoroboric acid or its derivatives in the same reaction.

Recent interest in this laboratory in the properties of hexafluorophosphoric acid (HPF_6) has prompted a reinvestigation of the Schiemann reaction[2] which involves the use of fluoroboric acid (HBF_4) or its derivatives for the conversion of aromatic amines to the corresponding fluorides according to the following sequence:

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(2) A. Roe, *Org. Reactions*, 193 (1949).