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.

Acknowledgment. It is a pleasure to acknowledge the help of John Bordley in the preparation of some of the intermediates used in this research while he served as a participant in the National Science Foundation Summer Research Program for Secondary School Students at the University of Florida. The work reported by this communication was supported in large part by W. R. Grace and Co. through a contract with the University of Florida.

GAINESVILLE, FLA.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF ESSEX COLLEGE, ASSUMPTION UNIVERSITY OF WINDSOR]

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

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Received June 12, 1961

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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(1) Supported by a Grant from the National Research Council of Canada and was presented at the 16th Southwest Regional Meeting of the American Chemical Society at Oklahoma City, Oklahoma, Dec. 3, 1960.

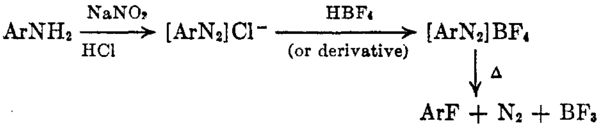
(2) A. Roe, *Org. Reactions*, 193 (1949).

TABLE I

HPF_6 *vs.* HBF_4 IN THE SCHIEMANN REACTION

	HBF_4 Method[a]			HPF_6 Method		
Aromatic Amine	Yield of ArN_2BF_4, %	Decomp. temp.	Yield of ArF, %	Yield of ArN_2PF_6, %	Decomp. temp.	Yield of ArF, %
o-Aminobenzoic acid	0–46	125	19 (9)[b]	79	129	78 (61)
p-Aminobenzoic acid	76–84	—	Failed	77	150	64 (49)
o-Bromoaniline	50	156	81 (40)	97	156	77 (75)
p-Bromoaniline	64	133	75 (52)	Quant.	144	(79)
p-Aminophenol	Failed	—	—	77	120–130	10–20
p-Chloroaniline	90	—	Not attempted	97	137	75 (73)
o-Aminoanisole	52–91	125	54–67	Quant.	120	(60)
p-Aminoanisole	85	139	67 (47)	Quant.	149	(70)
o-Nitroaniline	63–92	133	10–19	97	161	10–20
m-Nitroaniline	79–99	170–178	43–54	Quant.	—	(58)
p-Nitroaniline	80–100	156	40–58	Quant.	170	(63)
o-Aminotoluene	59–90	106	90	97	110	60 (58)
m-Aminotoluene	79–90	108	(87)	Quant.	110	(57)
p-Aminotoluene	67–90	110	(70)	97	112	(71)
2-Aminopyridine	Not isolated	<0	(34)	Not isolated	<−10	(33)

[a] Data from A. Roe *loc. cit.* [b] Numbers in parentheses represent over-all yields. Where appreciable ranges in yield are reported, no over-all yield is given.



$$ArNH_2 \xrightarrow[HCl]{NaNO_2} [ArN_2]Cl^- \xrightarrow[\text{(or derivative)}]{HBF_4} [ArN_2]BF_4 \xrightarrow{\Delta} ArF + N_2 + BF_3$$

The success of the Schiemann reaction *via* the fluoroborate method depends upon the isolation of the intermediate diazonium fluoroborate and the facile conversion of the dry salt to the aromatic fluoride. The scope of the method is limited by the relatively high solubility of the fluoroborates of amino-aromatic acids and aminophenols. Again, in our experience the pyrolysis step rarely results in better than 65–70% yield although higher yields have been reported. Presumably this is a result of side reactions caused by a combination of impurities and the presence of the powerful Lewis acid boron trifluoride in the hot reaction mixture.

It was felt that hexafluorophosphoric acid would be a more desirable reagent than fluoroboric acid since the intermediate aryldiazonium hexafluorophosphate salts (ArN_2PF_6), would be less soluble than the corresponding fluoroborates. This might permit more thorough washing to eliminate impurities without greatly affecting the yields. Also, decomposition according to the following equation

$$ArN_2PF_6 \xrightarrow{\Delta} Ar{-}F + N_2 + PF_5$$

yields phosphorus pentafluoride which is not as strong a Lewis acid as is boron trifluoride and side reactions should be minimized.

Lange and Mueller[3] reported the preparation of 4,4′-difluorobiphenyl and fluorobenzene by heating the corresponding diazonium hexafluorophosphate salts. A low yield was obtained for the difluorobiphenyl while no yield was reported for the fluorobenzene. This method has been given no further consideration in the literature until recently. Newman and Galt[4] reported the conversion of 6-bromo-2-naphthylamine and 1-bromo-3-naphthylamine to the fluoro analogues *via* the hexafluorophosphoric acid method. A slight increase in yield over the fluoroboric acid method was observed in both cases.

Several substituted aromatic amines were subjected to the Schiemann Reaction modified by the use of hexafluorophosphoric acid.[5] Comparisons with the use of fluoroboric acid or its derivatives can be seen in the chart.

In almost all cases, the yields of the ArN_2PF_6 salts were quantitative or nearly so. With the exception of the diazonium hexafluorophosphate salt derived from *p*-aminobenzoic acid, all could be washed liberally with cold water without appreciable loss. An appreciable increase in the yields of some aromatic fluorides with hexafluorophosphoric acid was observed over the fluoroboric acid method. Outstanding in this respect was the increase in the yields of *o*-fluorobenzoic acid (+52%), *p*-fluorobenzoic acid (+49%), *o*-fluorobromobenzene (+35%), *p*-fluorobromobenzene (+27%), *p*-fluoroanisole (+23%), and *p*-fluorophenol (+10–20%). A slight increase was observed for the *m*- and *p*-fluoronitroanilines while the *ortho* analog was obtained in both cases. With the exception of that salt derived from *p*-aminophenol, all other phosphorus hexafluoride salts had sharp melting points and compared favorably in most cases with boron tetrafluoride analogs.

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(3) W. Lange and E. Mueller, *Ber.*, **63**, 1058 (1930).

(4) M. S. Newman and R. H. B. Galt, *J. Org. Chem.*, **25**, 214 (1960). In this paper M. S. N. graciously acknowledged a previous communication from this laboratory.

(5) We wish to thank the Ozark-Mahoning Co. of Tulsa, Okla., for generous supplies of this acid.

EXPERIMENTAL

In the preparation of an ArN$_2$PF$_6$ salt, the amine was treated slowly with an excess of concentrated hydrochloric acid and water was added to effect solution. The solution was cooled by means of an ice-salt bath and held between 0 and −10°. Although some hydrochlorides would often crystallize in part when the temperature was lowered, solution occurred when diazotization proceeded. Diazotization was effected in the usual manner in the cold by the dropwise addition of a water solution containing a slight molar excess of sodium nitrite until an excess of nitrous acid was observed with starch-iodide paper.

While the solution was still cold, hexafluorophosphoric acid was added (about 20% excess) rapidly in one portion *via* a polyethylene container while the flask was swirled. Although the temperature would rise in some cases to as high as 30°, no appreciable effect on the yields was observed. The mixture was cooled again to 0–5° before filtration. The salts were washed with cold water. This was usually followed by washing with a mixture of a solution containing 80 parts ether and 20 parts methanol to facilitate drying. The salts were powdered and further dried *in vacuo* overnight.

Decomposition of the phosphorus hexafluoride salts was carried out in a hood in mineral oil whenever the product could be obtained *via* steam distillation procedure. A small amount of heavy mineral oil was placed in a three necked, round bottomed flask which was equipped with two spiral condensers (approx. 18 in.) and a Gooch rubber connecting tube through which the salt was introduced from an Erlenmeyer flask. The mineral oil was heated to a temperature slightly above the decomposition point of the salt which was then added portionwise such that a rapid release of phosphorus pentafluoride gas was observed. It was found desirable to decompose the salts as rapidly as possible to obtain best yields. After the last portion of salt was added, heating was continued for an additional 5 min. The reaction mixture was cooled rapidly and a 5% solution of sodium carbonate was poured slowly through the top of the condensers to wash down condensed fluorocarbon and neutralize the acidic reaction mixture. The product was then recovered by distillation with steam followed by separation, drying and final distillation.

The phosphorus hexafluoride salt from anthranilic acid was decomposed in xylene while those of *p*-aminobenzoic acid and *p*-aminophenol were decomposed dry. The following experimental details for the preparation of *o*-fluorobenzoic acid, *o*-fluorobromobenzene, and *p*-fluorobenzoic acid are included as exemplary of the varied decomposition techniques used in the hexafluorophosphoric acid method.

o-Fluorobenzoic acid. Anthranilic acid (41.1 g., 0.3 mole), in a 500-ml. Erlenmeyer flask, was dissolved in 210 ml. of a water solution which contained 30 ml. of concd. hydrochloric acid. The temperature of the solution was lowered to −5° with an ice-salt mixture whereupon the amine hydrochloride crystallized in part. Diazotization at this temperature with 26.4 g. (0.31 mole) of sodium nitrite dissolved in 75 ml. of water proceeded smoothly to yield a clear solution. While the temperature was maintained at −5°, hexafluorophosphoric acid (100 ml., 40% excess) was added in one portion with swirling. Although the temperature rose to 15° after addition, no evolution of gas resulted. Precipitation of the yellow diazonium hexafluorophosphate was instantaneous. Sometimes the precipitate dissolved and recrystallized on cooling again. To insure maximum yields, the temperature was again lowered to −5°. The precipitate was recovered by filtration, washed with 500 ml. of cold water and air dried, yield, 70.0 g. (79%), m.p. 129° dec.

Decomposition of the dry salt by free flame proved undesirable due to violent decomposition. However, when the salt was placed in xylene and heated to the decomposition point, evolution of gas occurred at a moderate rate. The dry salt was placed in a 500-ml., round bottomed, three-necked flask equipped with two 12-in. spiral condensers. Xylene was added and the flask was heated externally by means of an oil bath to 125° and maintained at this temperature until decomposition ceased as evidenced by very slow evolution of phosphorus pentafluoride. The xylene was boiled for 5 min. to expel excess gas. The reaction mixture was allowed to cool and the acid was extracted with a 5% sodium bicarbonate solution. After treatment with Norite, the sodium bicarbonate solution was poured slowly with stirring onto an excess of ice and concentrated hydrochloric acid whereupon the *o*-fluorobenzoic acid crystallized.

In a typical decomposition run of 20 g. (0.068 mole) of the dry fluorophosphate salt in 100 ml. of xylene, 7.4 g. (78%) of *o*-fluorobenzoic acid was obtained in a fairly pure state (m.p. 110–115°). Recrystallization from a chloroform–petroleum ether (b.p. 30–60°) solvent pair yielded the pure acid, m.p. 124–125° (recorded m.p. 120–122°), neut. equiv., 138.5.

o-Fluorobromobenzene. An aqueous hydrochloric acid solution prepared by mixing 95 ml. of concd. hydrochloric acid and 650 ml. of water was added slowly with stirring to 60 g. of *o*-bromoaniline (0.35 mole; EKC product, not redistilled) in a 2-l. Erlenmeyer flask. Solution was effected by heating on a steam bath. To the amine hydrochloride solution cooled to −10° in an ice-salt bath, a solution of sodium nitrite prepared by dissolving 29 g. (0.42 mole) in 75 ml. water was added with stirring at a rate to maintain the temperature below −5°. The excess of nitrous acid was detected with starch-iodide paper. To the cold diazonium solution, 74 ml. (1.4 moles) of 65% hexafluorophosphoric acid was added in one portion with swirling. Cooling and stirring was continued for an additional 30 min. before the separated diazonium hexafluorophosphate was isolated by suction filtration. The diazonium salt was washed in a Buchner funnel consecutively with 300 ml. of cold water and 400 ml. of a solution which contained 320 ml. of ether and 80 ml. of methanol. A slight yellow coloration was observed in the ether-methanol layer. Drying *in vacuo* of the filtered product overnight gave 111.1 g. (97%) of white *o*-bromobenzenediazonium hexafluorophosphate, m.p. 156° dec.

The dry powdered hexafluorophosphate salt was placed in a 250-ml. Erlenmeyer flask which was then attached to a 1-l., two necked, round bottomed flask by means of a short Gooch rubber connecting tube. Heavy mineral oil (300 ml.) was placed in the flask which was then fitted with a 20-in. spiral water-cooled condenser vented to a hood. The temperature of the mineral oil was raised by means of an external oil bath to 165° whereupon the salt was added rapidly in portions over a period of 30 min. The flask was cooled rapidly and 400 ml. of a 10% solution of sodium carbonate was added slowly. The product was isolated by steam distillation followed by separation and drying over sodium sulfate. Distillation from a Claisen-Vigreux flask produced 46.1 g. (75.5% over-all yield) of colorless *o*-bromofluorobenzene, b.p. 157°, n_D^{25} 1.5324.

p-Fluorobenzoic acid. An aqueous hydrochloric acid solution prepared by mixing 100 ml. of concd. hydrochloric acid and 240 ml. of water was added with stirring to 20 g. (0.146 mole) of *p*-aminobenzoic acid. The solution was cooled to −10° with an ice-salt bath and a solution of sodium nitrite prepared by dissolving 12 g. (0.17 mole) in 50 ml. of water was added with stirring at a rate to maintain the temperature below −5°. The excess of nitrous acid was detected with starch-iodide paper. The diazonium hexafluorophosphate salt was precipitated at once on the rapid addition of 20 ml. of 65% hexafluorophosphoric acid. The salt was recovered by suction filtration, air dried for several hours and finally dried overnight *in vacuo.* A yield of 33 g. (77%) was obtained, m.p. 128–130° dec.

The decomposition of the above salt was carried out in the dry state in an apparatus identical with that used for the decomposition of the *o*-bromobenzenediazonium hexafluorophosphate salt. The decomposition flask was lowered into a preheated oil bath (140°) and the salt was added rapidly in portions such that a rapid evolution of phosphorus pentafluoride was observed. When gas evolution ceased (15 min. over-all), the flask was cooled and the *p*-fluorobenzoic acid was recovered by extraction with a 5% sodium carbonate solution (150 ml.). The acid was precipitated when the basic solution was poured slowly with stirring into a mixture of ice and concentrated hydrochloric acid. After suction filtration and air-drying, the acid was recrystallized from a chloroform–petroleum ether (b.p. 30–60°) solvent pair. A yield of 64% (10 g.) of *p*-fluorobenzoic acid was obtained, m.p. 184–186°. A slight coloration can be removed by treating a chloroform solution of the acid with Norit.

WINDSOR, ONTARIO, CANADA

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DEPARTMENT, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO.]

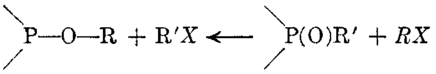
Phosphorus-Containing Monomers. II. The Synthesis and Polymerization of Dialkyl 2-Vinyloxyethylphosphonates [$CH_2{=}CHOCH_2CH_2P(O)(OR)_2$]

ROBERT RABINOWITZ

Received March 24, 1961

Synthetic routes to diethyl- and diisopropyl 2-vinyloxyethylphosphonate are described. These involve reaction of 2-chloroethyl vinyl ether with the corresponding tertiary phosphite. Low molecular weight polymers are obtained from these dialkyl 2-vinyloxyethylphosphonates using free radical techniques. Cationic polymerization failed completely.

Synthesis. The Michaelis-Arbuzov reaction is a classical method of forming a carbon-phosphorus bond.[1] Generally the tertiary phosphorus ester is heated with the alkyl halide between 100–150°, depending on the alkyl halide. A mixture of 2-chloroethyl vinyl ether and a small excess of triethyl phosphate was refluxed for ten days. Although no sign of reaction was apparent until the fifth day, a 50% yield of diethyl 2-vinyloxyethylphosphonate was obtained. No unchanged triethyl phosphite was recovered; instead diethyl ethylphosphonate, $C_2H_5P(O)(OC_2H_5)_2$ was found. It appeared that little reaction took place initially because the temperature was too low. As the low-boiling 2-chloroethyl vinyl ether was slowly consumed, the reflux temperature rose, increasing the rate. Also a factor in increasing the reflux temperature is the probable early formation of diethyl ethylphosphonate, either by thermal isomerization of the triethyl phosphite and/or by the reaction of ethyl chloride, prior to its escape as a gas, with triethyl phosphite. The reaction between triethyl phosphite and 2-chloroethyl vinyl ether in the presence of a large excess of tetralin, a high-boiling inert material, started immediately and was virtually completed in four days. A 74% yield of diethyl 2-vinyloxyethylphosphonate was obtained.



$$>P{-}O{-}R + R'X \longleftarrow >P(O)R' + RX$$

R and R' = alkyl

It appeared likely that, as triisopropyl phosphite was higher-boiling than triethyl phosphite, it could react with 2-chloroethyl vinyl ether in a reasonable amount of time without the use of a high-boiling inert solvent. Thus, by gradually adding the 2-chloroethyl vinyl ether to the refluxing phosphite, a 76% conversion to diisopropyl 2-vinyloxyethylphosphonate was obtained after four days.

Another well known procedure to prepare phosphonates is the reaction of the sodium salt of a dialkyl hydrogen phosphonate with a primary alkyl halide.[2,3] When diethyl sodium phosphonate

$$(RO)_2P(O)Na + R'CH_2X \longrightarrow NaX + (RO)_2P(O)R'$$

was mixed with 2-chloroethyl vinyl ether at 0° no reaction occurred. Refluxing overnight gave the expected sodium chloride. However, the only product noted was divinyl ether. Apparently the base,

$$NaP(O)(OC_2H_5)_2 + ClCH_2CH_2OCH{=}CH_2 \longrightarrow NaCl + HP(O)(OC_2H_5)_2 + (CH_2{=}CH)_2O$$

diethyl sodium phosphonate, dehydrochlorinates the ether at a rate much faster than that of the displacement reaction.

Hydrolysis. An effort was made to prepare the monoester of diethyl 2-vinyloxyethylphosphonate by the following hydrolytic reaction. The reaction had previously been demonstrated as a simple route to these monoesters when working with nonolefinic phosphonates.[4] Under either reflux

$$CH_2{=}CHOCH_2CH_2P(O)(OC_2H_5)_2 + OH^- \xrightarrow[\text{ethanol}]{H_2O\text{ or}} CH_2{=}CHOCH_2CH_2P(O)(OC_2H_5)O^-$$

or room temperature aqueous conditions, *no* monoester was noted.

Polymerization studies. Only a relatively small amount of information exists on the free radical

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[1] G. M. Kosolapoff, *Organophosphorus Compounds*, Wiley, New York, 1950, p. 121.

[2] B. C. Saunders, G. F. Stacey, F. Wild, and I. G. E. Wilding, *J. Chem. Soc.*, 699 (1948).

[3] G. M. Kosolapoff, *J. Am. Chem. Soc.*, **67**, 2259 (1945).

[4] R. Rabinowitz, *J. Am. Chem. Soc.*, **82**, 4564 (1960).