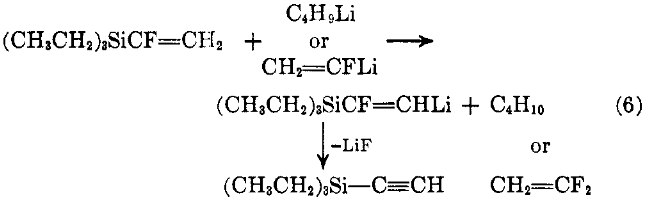
Reaction of 1-fluorovinyllithium with triethylchlorosilane gave triethylethynylsilane (30%) and not the expected triethyl(1-fluorovinyl)silane. The most likely route to this product involves initial formation of the expected product (eq 5). One of the terminal vinylic

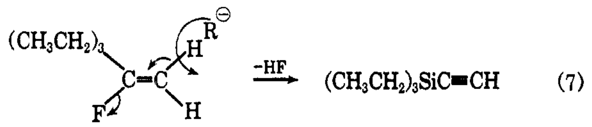
$$(CH_3CH_2)_3SiCl + CH_2{=}CFLi \longrightarrow \underset{\text{expected product}}{(CH_3CH_2)_3SiCF{=}CH_2} + LiCl \quad (5)$$

protons in this product is then exchanged as in eq 6



$$\begin{aligned}&(CH_3CH_2)_3SiCF{=}CH_2 + \overset{C_4H_9Li}{\underset{CH_2{=}CFLi}{\text{or}}} \longrightarrow \\ &\qquad (CH_3CH_2)_3SiCF{=}CHLi + C_4H_{10} \quad (6)\\ &\qquad \Big\downarrow{-LiF} \qquad\qquad\qquad\quad \text{or}\\ &\qquad \underset{\text{triethylethynylsilane}}{(CH_3CH_2)_3Si{-}C{\equiv}CH} \qquad CH_2{=}CF_2\end{aligned}$$

and subsequent elimination of lithium fluoride then gives triethylethynylsilane. This second step (eq 7) may more accurately be described as a concerted process resulting in the elimination of hydrogen fluoride in the presence of excess base.



A 1:1 mixture of *cis*- and *trans*-1,2-dichloro-1-fluoroethylene was treated with butyllithium and the resulting 1,2-dichloro-2-fluoro-vinyllithium was allowed to react with triethylchlorosilane. The normal substitution product, triethyl(1,2-dichloro-2-fluorovinyl)silane, was isolated in good yield (55%). No triethylfluorosilane was obtained. The product consisted of two geometric isomers in a ratio of 4:1. A similar isomer distribution was obtained on reaction of 1,2-dichloro-2-fluorovinyllithium with carbonyl compounds.[2]

Experimental Section[7]

The fluorine-containing vinyllithium reagents were prepared in ether as described previously.[2] Triethylchlorosilane (0.05 mole) was slowly added in ether (30 ml) to a cooled (−78°) solution of the lithium reagent in the same solvent (150 ml). The reaction mixture was stirred while it was warmed gradually (over 3 hr) to room temperature. Lithium chloride was normally precipitated between 0° and room temperature. The latter was removed by filtration and the solvent by distillation. The products were further purified by distillation followed by preparative-scale glpc. Physical properties and analyses of the compounds isolated are given in Table I.

Registry No.—Triethylchlorosilane, 994-30-9; **1,** 680-76-2; **2,** 15038-82-1; **3,** 358-43-0; **4,** 1777-03-3; **5,** 14897-57-5.

Acknowledgment.—We wish to acknowledge the financial support of the U. S. Army Natick Laboratory under DA 19-129-AMC-79[N] for this project. We are also grateful to Professor W. S. Brey, Jr., for the nmr analyses.

The Preparation of Some Phenoxaphosphine Derivatives by the Friedel-Crafts and Diazo Reactions[1]

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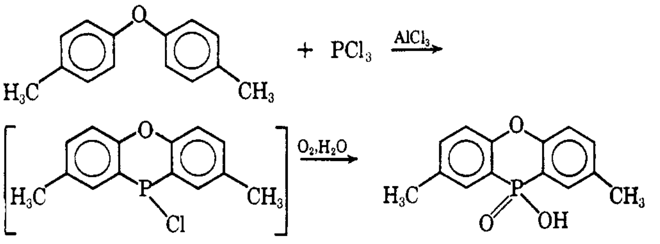
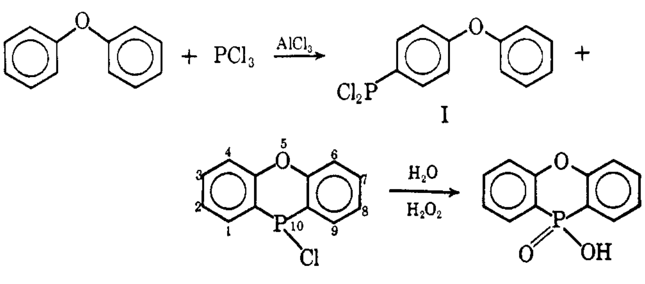
Although 10-chlorophenoxarsine[3] is easily prepared by refluxing phenyl ether with arsenic trichloride and a small quantity of aluminum chloride, the analogous reaction with phosphorus trichloride has been reported to yield only *p*-phenoxyphenyldichlorophosphine[4] (I). It seemed likely to us that some 10-chlorophenoxaphosphine (II) was also produced in this reaction and had been overlooked. Thus, phosphorus trichloride is known[5] to attack the *ortho* positions of *p*-tolyl ether and to give a good yield of a phenoxaphosphine derivative (III). In the present paper we are presenting evidence that 10-chlorophenoxaphosphine (II) is indeed formed in the reaction of phosphorus trichloride with phenyl ether. Thus, phenoxaphosphinic acid (IV) has been obtained in 2% yield from phenyl ether and phosphorus trichloride. A large amount of aluminum chloride (178 g/mole of phenyl ether) was employed in this reaction; under these conditions, the *p*-phenoxyphenyldichlorophosphine apparently undergoes further reaction to give undistillable products, while the 10-chlorophenoxaphosphine is relatively unaffected. When intermediate amounts of aluminum chloride were used, a mixture of products (probably *p*-phenoxyphenyldichlorophosphine and 10-chlorophenoxaphosphine) was obtained on distillation of the reaction mixture.



III



I

II

IV

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[7] Analyses were carried out by Galbraith Laboratories Inc., Knoxville, Tenn.

[1] Abstracted from the Ph.D. thesis of Jack B. Levy, North Carolina State University, 1967.

[2] University Chemical Laboratory, Cambridge University, Cambridge, England.

[3] W. L. Lewis, C. D. Lowry, and F. H. Bergeim, *J. Am. Chem. Soc.*, **43**, 891 (1921).

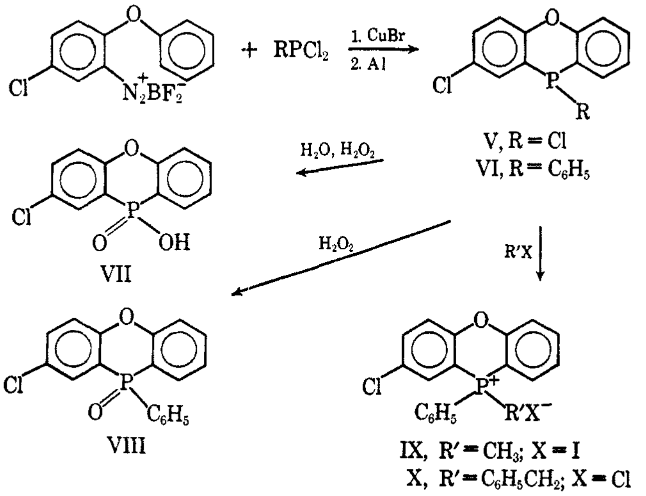
[4] W. C. Davies and C. J. O. R. Morris, *J. Chem. Soc.*, 2880 (1932).

[5] L. D. Freedman, G. O. Doak, and J. R. Edmisten, *J. Org. Chem.*, **26**, 284 (1961).

The Preparation of 2-Chloro-Substituted Phenoxaphosphine Derivatives by the Diazo Reaction.—We have previously reported the use of the diazo reaction for the preparation of certain heterocyclic organophosphorus compounds.[6,7] This method has been most successful when applied to the preparation of phenoxaphosphine derivatives. The method involves the reaction of a suitable diazonium tetrafluoroborate with phosphorus trichloride (or with an arylphosphonous dichloride) in the presence of cuprous bromide, reduction of the organophosphorus intermediate with aluminum, and isolation of the desired product by distillation. Starting with 2-phenoxybenzenediazonium tetrafluoroborate, we prepared 10-chlorophenoxaphosphine in 24% yield,[6] 10-phenylphenoxaphosphine in 26% yield,[7] and 10-*p*-tolyphenoxaphosphine in 19% yield.[7]

We have now extended the reaction to the preparation of ring-substituted phenoxaphosphines. Thus, 2,10-dichlorophenoxaphosphine (V) (Scheme I) and 2-chloro-10-phenylphenoxaphosphine (VI) were prepared in 30 and 31% yield, respectively. Compound V was converted almost quantitatively into 2-chlorophenoxaphosphinic acid (VII) by treatment with aqueous hydrogen peroxide, and VI was similarly converted into 2-chloro-10-phenylphenoxaphosphine 10-oxide (VIII). 2-Chloro-10-methyl-10-phenylphenoxaphosphonium iodide (IX) and 2-chloro-10-benzyl-10-phenylphenoxaphosphonium chloride (X) were also prepared from VI. We have not yet attempted to resolve these racemic phosphonium salts.

SCHEME I



Infrared Spectra.—The infrared spectra of phenoxaphosphine derivatives which contain a quadruply connected phosphorus (phenoxaphosphinic acids, phenoxaphosphine 10-oxides, and phenoxaphosphonium salts) have been found to contain three characteristic bands of medium to very strong intensity in the 1330–1215-cm^{-1} region. One band (medium to strong) appears at 1330–1320 cm^{-1}, the second (strong to very strong) appears at 1277–1268 cm^{-1}, and the third band (medium to strong) occurs at 1223–1215 cm^{-1}. The compounds examined include phenoxaphosphinic acid, 2-chlorophenoxaphosphinic acid, 2,8-dimethylphenoxaphosphinic acid,[5] 10-phenylphenoxaphosphine 10-oxide,[7] 10-*p*-tolylphenoxaphosphine 10-oxide,[7] 2-chloro-10-phenylphenoxaphosphine 10-oxide, 10-methyl-10-phenylphenoxaphosphonium iodide, 10-ethyl-10-phenylphenoxaphosphonium iodide, 10-benzyl-10-phenylphenoxaphosphonium chloride, 2-chloro-10-methyl-10-phenylphenoxaphosphonium iodide, and 2-chloro-10-benzyl-10-phenylphenoxaphosphonium chloride. This set of three bands has not been observed in closely related nonheterocyclic organophosphorus compounds nor in trivalent phenoxaphosphine derivatives. The phenoxaphosphine 10-oxides give an intense peak at 1200 cm^{-1} which is characteristic of the phosphoryl bond.

Experimental Section

General.—Melting points were taken on a Fisher-Johns apparatus with a thermometer calibrated against U.S.P. reference standards as previously described.[8] Infrared spectra were recorded on a Perkin-Elmer Model 521 spectrophotometer, and the samples were run in potassium bromide pellets. Nuclear magnetic resonance spectra were run on a Varian HA-100 spectrometer with a sweep width of 500 cps and with tetramethylsilane as an internal standard. Most of the analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. A few of the compounds were analyzed with an F & M carbon, hydrogen, nitrogen (CHN) analyzer, Model 185, by Mr. Roy L. Johnston of this department.

Phenoxaphosphinic Acid.—A 1-l. three-neck flask was fitted with a glass stopper, a sealed stirrer, and a reflux condenser. A larger rubber balloon filled with prepurified nitrogen and regulated by a two-way stopcock was connected to the top of the condenser. The flask was flamed and flushed with nitrogen. Phenyl ether (102 g, 0.60 mole), 330 g (2.4 moles) of phosphorus trichloride, and 107 g (0.80 mole) of anhydrous aluminum chloride were placed in the flask, and the resulting mixture was refluxed for 4 hr. The excess phosphorus trichloride was then removed by distillation. After the residue was cooled to 0°, 64.5 ml (0.80 mole) of pyridine[9] was added dropwise to the flask through a dropping funnel. Distillation at about 5 mμ then gave 50 g of phenyl ether (identified by its infrared spectrum) and 30 g of a second fraction (bp 135–150°). This fraction, which consisted largely of a complex of pyridine and aluminum chloride, was hydrolyzed and oxidized with alkaline hydrogen peroxide. The resulting solution on acidification gave a precipitate of phenoxaphosphinic acid. This melted at 230–233° after recrystallization from aqueous alcohol, and the melting point was not depressed upon admixture of the product with an authentic sample of phenoxaphosphinic acid.[6] The infrared spectra of the two samples were identical. The average yield was 3.0 g (2%).

Anal. Calcd for C$_{12}$H$_9$O$_3$P: C, 62.08; H, 3.91. Found: C, 62.15; H, 4.03.

2-Phenoxy-5-chlorobenzenediazonium Tetrafluoroborate.—This compound (mp 168° dec) was prepared by diazotization of 2-phenoxy-5-chloroaniline (Columbia Chemical Co.) in a 50% hydrogen tetrafluoroborate solution.

Anal. Calcd for C$_{12}$H$_8$BClF$_4$N$_2$O: C, 45.26; H, 2.53; N, 8.80. Found: C, 44.58; H, 2.52; N, 8.61.

2,10-Dichlorophenoxaphosphine.—2-Phenoxy-5-chlorobenzenediazonium tetrafluoroborate (31.0 g, 0.10 mole), 13.8 g (0.10 mole) of phosphorus trichloride, 100 ml of dry ethyl acetate, and 2.0 g of copper(I) bromide were allowed to react according to the procedure described for the preparation of 10-chlorophenoxaphosphine.[6] When the reaction began, there was a sudden change in the appearance of the suspended diazonium salt. The flask was immediately surrounded by cold water to moderate the reaction. When all of the diazonium salt had dissolved and the evolution of nitrogen was complete, the cold bath was removed. After 1 hr, powdered aluminum (1.8 g) was added and the mixture was then refluxed for 1 hr. Stirring was continued overnight. The usual isolation procedure[6] gave 8.0 g (30% yield)

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(6) G. O. Doak, L. D. Freedman, and J. B. Levy, *J. Org. Chem.*, **29**, 2382 (1964).

(7) J. B. Levy, G. O. Doak, and L. D. Freedman, *ibid.*, **30**, 660 (1965).

(8) G. O. Doak and L. D. Freedman, *J. Am. Chem. Soc.*, **73**, 5658 (1951).

(9) E. L. Gefter, *J. Gen. Chem. USSR*, **28**, 1398 (1958).

of 2,10-dichlorophenoxaphosphine (bp 135° at about 5 mμ), which melted at 120–122°.

Anal. Calcd for $C_{12}H_7Cl_2OP$: Cl, 26.35; P, 11.51. Found: Cl, 26.15; P, 11.54.

2-Chlorophenoxaphosphinic Acid.—2,10-Dichlorophenoxaphosphine was hydrolyzed and oxidized in an alkaline solution of hydrogen peroxide to give (after acidification) 2-chlorophenoxaphosphinic acid in 95% yield. After recrystallization the product melted at 240–242°.

Anal. Calcd for $C_{12}H_8ClO_3P$: Cl, 13.30; P, 11.62; neut equiv, 266.6. Found: Cl, 13.14; P, 11.49; neut equiv, 267.7.

2-Chloro-10-phenylphenoxaphosphine.—2-Phenoxy-5-chlorobenzenediazonium tetrafluoroborate (31.0 g, 0.10 mole), 100 ml of anhydrous ethyl acetate, 17.9 g (0.10 mole) of phenylphosphonous dichloride (Eastman P6544), and 2.0 g of copper(I) bromide were allowed to react according to the procedure described for the preparation of 2,10-dichlorophenoxaphosphine. After the evolution of nitrogen was complete, the mixture was allowed to stir for 1 hr. Powdered aluminum (1.8 g) was then added to the flask. The mixture was refluxed for 1 hr and was stirred overnight. The usual isolation procedure gave 9.6 g (31%) of 2-chloro-10-phenylphenoxaphosphine (bp 160° at about 5 mμ). The product, which was recrystallized from aqueous alcohol with the aid of a seed crystal of 10-phenylphenoxaphosphine, had a melting point of 41.5–42.0°.

Anal. Calcd for $C_{18}H_{12}ClIOP$: Cl, 11.41; P, 9.97. Found: Cl, 11.54; P, 9.84.

2-Chloro-10-phenylphenoxaphosphine 10-Oxide.—2-Chloro-10-phenylphenoxaphosphine was oxidized in an alkaline solution of aqueous ethanol with hydrogen peroxide to give a 98% yield of 2-chloro-10-phenylphenoxaphosphine 10-oxide. The melting point was 150–151° after recrystallization from a mixture of ethanol and 6 *N* hydrochloric acid. A crystal of 10-phenylphenoxaphosphine 10-oxide was used for seeding.

Anal. Calcd for $C_{18}H_{12}ClO_2P$: Cl, 10.85; P, 9.48. Found: Cl, 10.87; P, 9.48.

2-Chloro-10-methyl-10-phenylphenoxaphosphonium Iodide.—2-Chloro-10-phenylphenoxaphosphine and a slight excess of methyl iodide were heated in a sealed tube at 100° for 4 hr. The product was recrystallized from a mixture of ethanol and petroleum ether (bp 30–60°); mp 238.0–240.5°, yield 72%. The nmr spectrum of the compound dissolved in deuteriochloroform displayed absorption at τ 6.61 (doublet, $J_{PCH} = 14.5$ cps) owing to the methyl group.

Anal. Calcd for $C_{19}H_{15}ClIOP$: C, 50.42; H, 3.34. Found: C, 50.57; H, 3.47.

2-Chloro-10-benzyl-10-phenylphenoxaphosphonium Chloride.—2-Chloro-10-phenylphenoxaphosphine and a slight excess of benzyl chloride were heated at 100° for 4 hr. The product, which was recrystallized from a mixture of ethanol and petroleum ether, did not melt below 300°. The yield of 2-chloro-10-benzyl-10-phenylphenoxaphosphonium chloride was 41%. The nmr spectrum of the compound in trifluoroacetic acid displayed absorption at τ 5.60 (doublet, $J_{PCH} = 13.6$ cps) owing to the methylene protons.

Anal. Calcd for $C_{25}H_{29}Cl_2OP$: Cl, 15.85; P, 6.92. Found: Cl, 15.98; P, 7.11.

10-Methyl-10-phenylphenoxaphosphonium Iodide.—10-Phenylphenoxaphosphine was dissolved in an excess of methyl iodide, and the resulting solution was allowed to stand overnight in a stoppered flask. The precipitated product (85%) melted at 244–245° (lit.[10] mp 236–237°). The nmr spectrum in deuteriochloroform displayed absorption owing to the methyl group at τ 6.65 (doublet, $J_{PCH} = 13.7$ cps).

Anal. Calcd for $C_{19}H_{16}IOP$: C, 54.57; H, 3.86. Found: C, 54.41; H, 3.78.

10-Ethyl-10-phenylphenoxaphosphonium Iodide.—10-Phenylphenoxaphosphine and a slight excess of ethyl iodide were heated in a sealed tube at 100° for 2 hr. After recrystallization from ethanol–petroleum ether, the product melted at 255–257°; yield, 55%. The nmr spectrum in deuteriochloroform displayed absorption at τ 6.11 (two quartets, $J_{PCH} = 12.3$ cps and $J_{HCCH} = 7.3$ cps) owing to the methylene group and absorption at τ 8.87 (two triplets, $J_{PCCH} = 22.2$ cps) owing to the methyl group.

Anal. Calcd for $C_{20}H_{18}IOP$: P, 7.17. Found: P, 7.20.

10-Benzyl-10-phenylphenoxaphosphonium Chloride.—10-Phenylphenoxaphosphine was dissolved in a large excess of benzyl chloride, and the resulting solution was allowed to stand in a stoppered flask for 4 days. The precipitated product (50%) was removed by filtration and washed with carbon tetrachloride; mp >300°. The nmr spectrum in trifluoroacetic acid displayed absorption at τ 5.60 (doublet, $J_{PCH} = 13.7$ cps).

Anal. Calcd for $C_{25}H_{19}Cl_2OP$: C, 74.54; H, 5.00; Cl, 8.80; P, 7.69. Found: C, 74.45; H, 5.09; Cl, 8.92; P, 7.45.

Registry No.—IV, 15042-79-2; V, 15042-80-5; VI, 15042-81-6; VII, 15040-61-6; VIV, 15040-62-7; IX, 15040-63-8; X, 15040-64-9; 10-methyl-10-phenylphenoxaphosphonium iodide, 15040-65-0; 10-ethyl-10-phenylphenoxaphosphonium iodide, 15040-66-1; 10-benzyl-10-phenylphenoxaphosphonium iodide, 15040-67-2.

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[10] F. G. Mann and I. T. Millar, *J. Chem. Soc.*, 3746 (1953).

Nitrile Oxides. X. An Improved Method for the Preparation of Nitrile Oxides from Aldoximes[1]

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Received August 10, 1967

It was recently reported that nitrile oxides could be prepared by dehydrogenation of the corresponding aldoximes with alkali hypohalogenites, preferably sodium hypobromite, in alkaline aqueous solution.[2] Yields were generally very satisfactory with aromatic monoaldoximes bearing no functional substituents on the aromatic ring, but they decrease sharply when the method was extended to dialdoximes or heterocyclic aldoximes particularly if the molecule contained an additional tertiary amino group.[1]

We have now found that N-bromosuccinimide (NBS) in N-dimethylformamide (DMF) solution is a superior dehydrogenating agent for the conversion of aldoximes into nitrile oxides. Other N-halogenated compounds, such as N-bromophthalimide or N-chloro-*p*-toluenesulfonamide, gave less favorable results. Base (1 mole) is also necessary to complete the reaction. If the oxime and the nitrile oxide were both relatively stable species, it made no difference whether the base was added first and then the NBS or *vice versa.* In the latter case, the reaction apparently proceeded first to the hydroximic acid bromide which was subsequently dehydrobrominated by the base to the nitrile oxide. If the aldoxime, however, contained other groups sensitive to attack by NBS the former procedure might lead to undesirable products resulting from additional bromination.[3] As bases, sodium methylate or triethylamine were used in most cases with equal success. Since, however, triethylamine is attacked by NBS, it is preferable to add the NBS to the oxime prior to the introduction of the amine. At temperatures between 5 and 15°, the reaction was always complete within 1 hr. Dilution of the reaction mixture with water precipitated the nitrile oxide, often almost analytically pure, while the formed succinimide stayed in solution.

Our results (in comparison with the other method where data were available) are compiled in Table I.

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(1) Previous communication by C. Grundmann and R. Richter, *J. Org. Chem.*, **32**, 2308 (1967).

(2) C. Grundmann and J. M. Dean, *ibid.*, **30**, 2809 (1965).

(3) For example, Table I, **7** and **9**, and footnotes *g* and *j*.