

The infrared spectrum of the last fraction and that of pyrrole were identical. Gas phase chromatography at 148° and at 130° using a Silicone column showed peaks which had the same retention times as those of an authentic sample of pyrrole.

Attempted reaction of N-trimethylsilylpyrrole with ethanol. In a 10-ml. Erlenmeyer flask were placed 116 mg. of *N*-trimethylsilylpyrrole and 2.0 ml. of ethanol (containing less than 1% water), and the mixture was swirled for 1 min. A 0.005-ml. aliquot was removed and injected into the gas phase instrument (Silicone column, T = 110°). Only one peak, which had the same retention time as that of *N*-trimethylsilylpyrrole was observed. The ethanol mixture was then heated under reflux for 1 hr., after which time another 0.005-ml. aliquot was injected into the gas phase instrument. This time two peaks were detected, the major one having the same retention time as the *N*-trimethylsilylpyrrole and the second (shorter retention time) the same as that of pyrrole; however, the area of the pyrrole peak was only 0.12% of the total area of the two peaks. The mixture was allowed to stand 3 days at which time the area under the pyrrole peak was 0.14% of the total area. No other compounds, besides ethanol, were detected in any of the gas chromatograms.

Reaction with aqueous ethanol. In a 10-ml. Erlenmeyer flask were placed 56 mg. of *N*-trimethylsilylpyrrole, 1.0 ml. of ethanol, and 0.5 ml. of water. After 15 min. a 0.005-ml. aliquot was removed and injected into the gas phase instrument (Silicone column, T = 110°). The major peak was that of *N*-trimethylsilylpyrrole. A small deflection in the baseline having the same retention time as pyrrole was detected; however, the area was too small for an area comparison. After the solution had been heated under reflux for 30 min., the pyrrole peak had increased to 19.5% of the total, and after 1 hr., 29%.

Acid-catalyzed reaction. In a 10-ml. Erlenmeyer flask were placed 110 mg. of *N*-trimethylsilylpyrrole, 2.0 ml. of ethanol and 1 drop of concentrated hydrochloric acid. The solution was swirled and, in less than 1 min. after the initial mixing, a 0.005-ml. aliquot was injected into the gas phase instrument (Silicone column, T = 105°). Three peaks were observed: peak 1, retention time, 0.80 min., area, 22%; peak 2, retention time, 12.0 min., area, 30%; and peak 3, retention time, 1.60 min., area, 48%. Under the same conditions, pyrrole had a retention time of 1.60 min. and *N*-trimethylsilylpyrrole, 5.20 min. No trace of the *N*-trimethylsilylpyrrole could be detected. Peak 2 had the same retention

time as a sample of trimethylethoxysilane prepared from trimethylchlorosilane and ethanol.

Base-catalyzed reaction. In a 10-ml. Erlenmeyer flask were placed 71 mg. of *N*-trimethylsilylpyrrole and 1.0 ml. of ethanol. To this solution was added 4 mg. of potassium hydroxide (in ethanol) and the mixture was swirled for 1 min., then a 0.005 ml. aliquot was injected into the gas phase instrument (Silicone column, T = 105°). Two major peaks were observed and the trace of a third was detected; peak 1, retention time, 0.04 min., trace; peak 2, retention time, 0.74 min., 51%; peak 3, retention time, 1.56 min., 48%. Under the same conditions, the retention time for pyrrole was 1.57 min. and the time for *N*-trimethylsilylpyrrole was 5.15 min. No deflection in the base line could be detected at 5.15 min., indicating the absence of the *N*-silylpyrrole. Peak 2 had the same retention time as a sample of trimethylethoxysilane prepared from trimethylchlorosilane and ethanol.

Attempted thermal rearrangement of N-trimethylsilylpyrrole. One gram of *N*-trimethylsilylpyrrole was sealed in a glass tube and heated at 225° for 17 hr. By the end of the heating period the material had undergone extensive charring. An aliquot of the liquid remaining was analyzed using gas phase chromatography (Silicone column, T = 110°), and only one peak (*N*-silylpyrrole) could be detected.

Another attempt was made, using diphenyl ether as solvent. A mixture of 10 ml. of diphenyl ether (b.p. 259°) and 1.0 g. of *N*-trimethylsilylpyrrole was heated under reflux for 12 hr. No charring was observed. Gas phase analysis of the reaction mixture indicated that the *N*-silylpyrrole had not undergone rearrangement. Only peaks corresponding to the *N*-silylpyrrole and the diphenyl ether were detected. *N*-Trimethylsilylpyrrole was isolated from the reaction mixture using the gas phase instrument; its infrared spectrum was identical with that of the starting *N*-silylpyrrole.

Tetrapyrrolylsilane (II). To 0.2 mole of potassium pyrrole in 150 ml. of ether and 75 ml. of benzene was added 0.05 mole of silicon tetrachloride over a 30-min. period, and the mixture was heated under reflux for 45 min. The potassium chloride was filtered from the mixture and the solution was allowed to stand overnight. The white, needle-like crystals which formed were filtered and recrystallized from benzene to yield 0.7 g. (4.5%) of tetrapyrrolylsilane (II), m.p. 167.5–168.5° (lit.,²⁸ m.p. 173°).

SAN JOSE, CALIF.

(28) Ref. 9(a).

[CONTRIBUTION NO. 11 FROM THE EXPLORATORY RESEARCH LABORATORY OF DOW CHEMICAL OF CANADA, LIMITED]

Organophosphorus Compounds. VII.^{1a} Alkyl- and Arylphosphorodihalidothioates Containing Fluorine

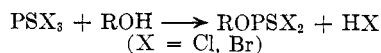
G. A. OLAH AND A. A. OSWALD^{1b}

Received August 24, 1959

O-Alkyl- and *O*-arylphosphorodifluoridothioates were prepared from phosphorus thiohalides with alcohols and phenols. *O*-Arylphosphorochlorofluoridothioates were prepared from phosphorus thiodichlorofluoride and phenols.

The synthesis of *O*-alkylphosphorodihalidothioates were first reported by Pistschimuka^{2,3} and in-

volved the reaction of phosphorus thiochloride or bromide with an alcohol:^{4,5,6}



(1a) Part VI, *J. Org. Chem.*, **24**, 1443 (1959).
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(2) P. Pistschimuka, *Ber.*, **41**, 3854 (1908).

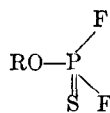
(3) P. Pistschimuka, *J. Russ. Phys. Chem. Soc.*, **44**, 1406 (1912).

(4) V. M. Plets, *Zhur. Obschei Khim.*, **6**, 1198 (1936).

(5) V. M. Plets, *Zhur. Obschei Khim.*, **8**, 1296 (1938).

(6) T. W. Martin, G. R. Norman, E. A. Weilmuenster, *J. Am. Chem. Soc.* **70**, 2523 (1948).

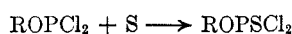
TABLE I
O-ALKYLPHOSPHORODIFLUORIDOTHIOATES AND *O*-ARYLPHOSPHORODIFLUORIDOTHIOATES



R	Yield (%)	B.P. (C./mm.)	n_D^{20}	Fluorine	
				Calcd.	Found
Ethyl	63	78-78.5/760 ^a	1.3942	26.00	25.65
Isopropyl	60	88-89/760	1.3813	23.57	23.35
<i>t</i> -Butyl	61	47-48/20	1.3889	22.32	22.49
Cyclohexyl	72	42-43/5	1.4408	18.98	19.06
Phenyl	82	52-52.5/14	1.4869	19.56	19.71
<i>o</i> -Cresyl	85	59-60/10	1.4849	18.25	18.42
<i>o</i> -Nitrophenyl	68	118-120/8	1.5389	15.88	15.94
<i>p</i> -Chlorophenyl	84	52/4	1.5033	16.62	16.81
α -Naphthyl	81	82-83/2	1.5704	15.55	15.27

^a Booth and co-workers⁷ reported b.p. 78.4°.

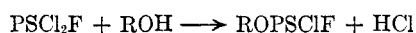
According to another method which has been used to a lesser extent, sulfur was added to alkylphosphorodichloridites⁵ to yield alkylphosphorodichloridothiathates:



The synthesis of an alkylphosphorodihalidothioate containing fluorine was accomplished first by Booth and his co-workers,⁷ who achieved a fluorine exchange in the case of ethylphosphorodichloridothioate by using antimony trifluoride.



The present authors⁸ previously reported the preparation of alkylphosphorochlorofluoridothioates by the reaction of phosphorus thiodichlorofluoride and alcohol.



Of the *O*-arylphosphorodihalidothioates, only the *O*-arylphosphorodichloridothioates were investigated in detail. Methods, including the reaction of phosphorus thiochloride with a basic aqueous solution of a phenol,^{9,10} addition of sulfur to *O*-arylphosphorodichloridites at elevated temperatures^{11,12,13} and reacting a phenol, phosphorus thiochloride, and pyridine as the acid binding agent¹⁴ were used for their synthesis.

O-Phenylphosphorodibromidothioates were also synthesized.

(7) H. S. Booth, D. R. Martin, F. E. Kendall, *J. Am. Chem. Soc.*, **70**, 2523 (1948).

(8) G. A. Olah, A. A. Oswald, *Liebigs Ann. Chem.*, **602**, 118 (1957).

(9) W. Autenrieth, O. Hildebrand, *Ber.*, **31**, 1094 (1898).

(10) W. Autenrieth, W. Meyer, *Ber.*, **58**, 840 (1925).

(11) R. Anschutz, W. O. Emery, *Ann.*, **253**, 117 (1889).

(12) W. Strecker, C. Grossman, *Ber.*, **49**, 64 (1916).

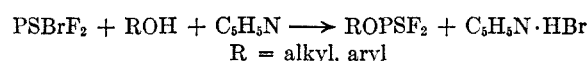
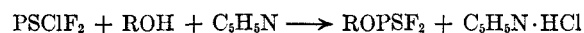
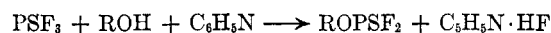
(13) F. Ephraim, *Ber.*, **44**, 3414 (1911).

(14) L. R. Drake and co-workers (Dow Chemical Co.) U. S. Patent 2,552,537 and 2,552,541.

No arylphosphorodihalidothioates containing fluorine were known at the time the present investigation was undertaken.

In this paper, the reaction of various phosphorus thiohalides containing fluorine with alcohols and phenols is described. These reactions yielded alkyl- and arylphosphorodihalidothioates containing fluorine.

At first the reaction of phosphorus thiofluoride, phosphorus thiochlorodifluoride, and phosphorus thiobromodifluoride with equimolar amounts of alcohols and phenols was studied, in the presence of pyridine as an acid binding agent. Alkyl- and arylphosphorodifluoridothioates were obtained according to the following general reaction equations:



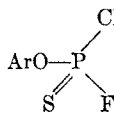
Some characteristic physical and analytical data of the prepared compounds are given in Table I.

The ethyl-, isopropyl-, *t*-butyl-, cyclohexylphosphorodifluoridothioates are colorless liquids. They fumed in air to some extent depending on their vapor pressure and were immiscible with water, although on standing they underwent aqueous hydrolysis.

The phenyl-, *o*-cresyl-, *o*-nitrophenyl-, *p*-chlorophenyl-, and α -naphthylphosphorodifluoridothioates are liquids immiscible with water and are colorless with one exception—the yellow *o*-nitrophenylphosphorodifluoridothioate.

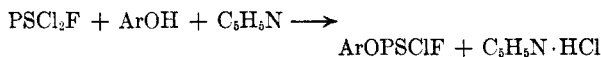
In the presence of oxygen both the alkyl- and the arylphosphorodifluoridothioates are oxidized with the production of sulfur dioxide. The presence of sulfur dioxide leads to the formation of red colored decomposition products.

In the following part of the work *O*-arylphosphorochlorofluoridothioates were prepared starting from phosphorus thiodichlorofluoride and phenols.

TABLE II
 O-ARYLPHOSPHOROCHLOROFLUORIDOTHIOATES


Ar	Yield (%)	B.P. (°C/mm.)	n_D^{20}	Cl %		F %	
				Calcd.	Found	Calcd.	Found
Phenyl	85	60.5-61/5	1.5290	16.83	17.07	9.02	9.06
<i>o</i> -Cresyl	84.5	89-90/8	1.5274	15.78	16.04	8.45	8.68
<i>m</i> -Cresyl	88	103-104/8	1.5251	15.78	15.62	8.45	8.23
<i>p</i> -Cresyl	87	99-100/8	1.5260	15.78	15.49	8.45	8.36
<i>m</i> -Methoxyphenyl	81	110-111/8	1.5345	14.73	14.47	7.89	7.73
<i>p</i> -Chlorophenyl	85	100.5-101/7	1.5449	28.93	28.93	7.75	7.56
<i>p</i> -Nitrophenyl	70.5	119-120/5	1.5641	13.86	13.86	7.43	7.66
α -Naphthyl	77	116-117/4	1.6061	13.60	13.31	7.28	7.21
β -Naphthyl	75	118-119/3	1.6062	13.60	13.53	7.28	6.85

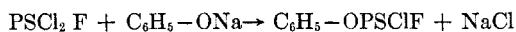
Because of the decreased reactivity of phenols as compared to alcohols, pyridine was used to bind the hydrochloric acid formed:



In this manner the phenyl-, *o*-cresyl-, *m*-cresyl-, *p*-cresyl-, *p*-chlorophenyl, *p*-nitrophenyl-, *m*-methoxyphenyl-, α -naphthyl-, α -naphthylphosphorochlorofluoridothioates were obtained. The yields were almost quantitative. No considerable amounts of diarylphosphorofluoridothioates were formed in the preparation of any of the above mentioned derivatives. Pyridine could be replaced by other tertiary amines, such as dimethylaniline or triethylamine, which forms ammonium salts with the hydrochloric acid formed in a similar manner. Some characteristic physical and analytical data of the compounds are given in Table II.

The *O*-arylphosphorochlorofluoridothioates are liquids immiscible with water and have a slightly acrid odor. They can be distilled in vacuum without decomposition and are colorless except for *p*-nitrophenylphosphorochlorofluoridothioate which is light yellow.

The reaction of phosphorus thiochloride with basic aqueous phenolates gave in several cases only diarylphosphorochloridothioates, or triarylphosphorothioates.¹ Phosphorus thiodichlorofluoride, however, reacted with an aqueous solution of sodium phenolate to yield 62% phenylphosphorochlorofluoridothioate:



EXPERIMENTAL

Absolute solvents and anhydrous reagents were used in all cases except for the reaction with aqueous sodium phenolate. During the course of the experiments the necessary precautions were taken to protect the reagents and the product from moisture.

O-Alkylphosphorodifluoridothioates. A mixture of 15 g. (0.11 mole) of phosphorus thiochlorodifluoride (or the equivalent amount of phosphorus thiofluoride or phosphorus thio-

bromodifluoride) and 100 ml. of ether was stirred and cooled in a Dry Ice-acetone bath to -78° . To the cool solution 20 ml. ether solution of 0.1 mole of alcohol and 8.3 g. (0.105 mole) of pyridine was added dropwise. During the addition the temperature of the reaction mixture did not rise above -60° . Then the reaction mixture was allowed to reach room temperature while the stirring was continued. The pyridine hydrochloride, which had precipitated, was filtered off by suction and washed with 15 ml. ether. On distilling the combined filtrates, the solvent was removed first, then the crude product which remained was fractionated. In the case of the alkylphosphorodifluoridothioates prepared from *t*-butyl and cyclohexyl alcohols, the fractionation was carried out in vacuum. The yields and some physical and analytical data of the pure compounds may be found in Table I.

O-Arylphosphorodifluoridothioates. To a solution of 15 g. (0.11 mole) of phosphorus thiochlorodifluoride (or the equivalent amount of phosphorus thiofluoride or phosphorus thiochlorodifluoride) and 0.1 mole of the corresponding phenol in 100 ml. of toluene, 8.3 g. (0.105 mole) of pyridine in 30 ml. of toluene was added dropwise while stirring and cooling the mixture with Dry Ice-acetone. The temperature of the reaction mixture did not exceed -50° during the addition. While the stirring was continued, the reaction mixture was allowed to come to room temperature and to stand 2 hr. until completion of the reaction. The work up of the products followed a procedure analogous to that mentioned above for alkylphosphorodifluoridothioates. The yields and physical and analytical data of the compounds obtained are shown in Table I.

O-Arylphosphorochlorofluoridothioate. To a solution of 16.7 g. (0.11 mole) of phosphorus thiodichlorofluoride in 20 ml. of benzene a solution of 94 g. (0.1 mole) of the corresponding phenol in 30 ml. benzene was added. Then to the resulting mixture 7.9 g. (0.1 mole) of pyridine diluted with 20 ml. of benzene was added dropwise at room temperature with water cooling and stirring. The reaction mixture was kept for an additional half hour at room temperature and then for another half hour at 40° in order to complete the reaction. The pyridine hydrochloride precipitate was filtered with suction and washed with benzene. The combined filtrates were fractionated *in vacuo* after removal of the benzene at atmospheric pressure. The yields of compounds and their physical and analytical data are given in Table I.

Using dimethylaniline as the acid binding agent a yield of 74%, with triethylamine 81%, of *O*-phenylphosphorochlorofluoridothioate was obtained. In the case of dimethylaniline, the hydrochloride was difficult to filter and was therefore removed by washing with water.

Preparation of O-phenylphosphorochlorofluoridothioate with aqueous sodium phenolate. A solution of 9.4 g. (0.1 mole) of

phenol in 82 ml. of 5% aqueous sodium hydroxide was added dropwise to 16.7 g. (0.11 mole) of phosphorus thiodichlorofluoride with shaking and water-cooling. The reaction mixture was stirred for an additional half hour and then allowed to stand at room temperature. The oil which separated was dissolved in 50 ml. of benzene and washed with 1.5% aqueous sodium hydroxide solution until neutral. The ben-

zene phase was dried over sodium sulphate, then the solvent was removed and the residual liquid fractionated in vacuo. Phenylphosphorochlorofluoridothioate, $n_D^{20} = 1.5298$, was obtained between 60–61°/5 mm. in 62% yield.

Anal. Calcd. Cl, 16.83; F, 9.02. Found: Cl, 16.45; F, 9.05.

SARNIA, ONT., CANADA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

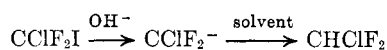
Methylene Derivatives as Intermediates in Polar Reactions. XX. The Reactions of Aqueous and Alcoholic Base with Chlorodifluoromethane and Difluoroiodomethane¹

JACK HINE AND ARTHUR D. KETLEY

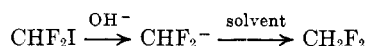
Received September 2, 1959

We have reinvestigated a report that with 15% potassium hydroxide in ethanol for forty-eight hours at 35°, chlorodifluoromethane, chlorodifluoroiodomethane, and difluoroiodomethane gave no reaction, 24% chlorodifluoromethane, and 19% difluoromethane, respectively. It was found that chlorodifluoroiodomethane reacts essentially completely with ethanolic potassium hydroxide within a few minutes and that difluoroiodomethane yields no more than 5%, if any, difluoromethane. Rate constants were determined for the reaction of difluoroiodomethane with hydroxide ion in aqueous solution. From the results obtained it appears that the reaction is initiated by a concerted α -dehydroiodination to yield difluoromethylene directly in one step.

Haszeldine has reported that chlorodifluoromethane is stable to the action of 15% potassium hydroxide in 95% ethanol for forty-eight hours at 35°,² and that under the same conditions chlorodifluoroiodomethane yields 24% chlorodifluoromethane and that difluoroiodomethane yields 19% difluoromethane. Our observations that chlorodifluoromethane is quite reactive toward aqueous alkali,³ sodium methoxide⁴ and potassium isopropoxide⁵ caused us to doubt the first two reports. For the latter two reported reactions the mechanisms



and



were suggested.² In view of our evidence that attempts to generate the chlorodifluoromethyl anion instead bring about the concerted formation of the intermediate difluoromethylene and thence its reaction products,^{3,6} the reaction reported for chlorodifluoroiodomethane seemed improbable, and in view of our observation that α -fluorine is the least effective of the α -halogen substituents at

facilitating carbanion formation⁷ we doubted the formation of a methylene halide reported from difluoroiodomethane (but not chlorofluoroiodomethane nor fluorodiodomethane). We have therefore reinvestigated some of these points and also carried out some related experiments of interest.

RESULTS AND DISCUSSION

When solutions of chlorodifluoromethane and potassium hydroxide in ethanol are mixed at 35°, a copious precipitate of potassium chloride is formed within minutes. Titrations revealed that the theoretical amount of chloride ion ($\pm 5\%$) was formed within 5 minutes. This observation makes the report of a 24% yield of chlorodifluoromethane formed (from chlorodifluoroiodomethane) after 48 hours in ethanolic potassium hydroxide² difficult to understand.

The volatile products of the reaction of difluoroiodomethane with ethanolic potassium hydroxide were studied in a number of runs. Fluoriform, ethyl difluoromethyl ether, and varying amounts of starting materials were found, but no clear evidence for methylene fluoride formation could be obtained. Experiments with authentic methylene fluoride showed that not more than about 5% could have been formed and remained undetected.

In order to learn more about the mechanism of the reaction of difluoroiodomethane with base the kinetics of the reaction with aqueous sodium hydroxide were studied. This haloform proved to be

(1) This work was supported in part by the U. S. Atomic Energy Commission. For the preceding article in this series see J. Hine, A. D. Ketley, and K. Tanabe, *J. Am. Chem. Soc.*, in press.

(2) R. N. Haszeldine, *J. Chem. Soc.*, 4259 (1952).

(3) J. Hine and P. B. Langford, *J. Am. Chem. Soc.*, **79**, 5497 (1957).

(4) J. Hine and J. J. Porter, *J. Am. Chem. Soc.*, **79**, 4403 (1957).

(5) J. Hine and K. Tanabe, *J. Am. Chem. Soc.*, **80**, 3002 (1958).

(6) J. Hine and D. C. Duffey, *J. Am. Chem. Soc.*, **81**, 1131 (1959).

(7) J. Hine, N. W. Burske, M. Hine, and P. B. Langford, *J. Am. Chem. Soc.*, **79**, 1406 (1957).