Experimental Section

Materials.—The oxygen difluoride was purchased from Allied Chemical Co. and used without further purification (<1% CO_2). The olefins were obtained from commercial sources and their physical constants were compared with established values to ensure purity. The perfluoro olefins were checked for purity by vapor phase chromatography.

Apparatus.—The oxygen difluoride was stored in large-volume glass bulbs which were an integral part of a standard high-vacuum line. All mercury manometers were protected with a layer of degassed Kel-F KF-10[6] oil and stopcocks were lubricated with Kel-F No. 90[6] grease. Other lubricants are *not* acceptable. The OF_2 can be stored in Pyrex indefinitely without decomposition if the above precautions are taken.

Reaction of the Perfluoro Olefins with OF_2.—The perfluoro olefin additions were conducted by mixing measured quantities of reactants in 500-cc. Pyrex bulbs and irradiating with a high-pressure mercury flood lamp.[7] The bulb was cooled with an air stream to avoid overheating and the temperature was maintained at 35° with the lamp 6 in. from the bulb. As all the additions were performed in a similar manner, only the procedure for perfluoropropylene, given below, will be described in detail. The perfluoropropylene (6.24 mmoles) was admixed with 7.67 mmoles of OF_2 and irradiated for 12 hr. At the end of this period the contents were vacuum distilled and separated into fractions which condensed at −126 and −196°. The total content of the fractions in millimoles was determined by expanding into a known volume and determining the pressure. The −126° condensable fraction contained a total of 6.17 mmoles. Analysis by vapor phase chromatography (15 ft. × 0.25 in., 30% FC-43[8] at 10°) indicated three components.

Compound A (43%, 2.68 mmoles) was purified by chromatography and identified as perfluoropropane by comparison of its infrared and mass spectra with those of an authentic sample. Compound B (42%, 2.56 mmoles) after isolation by chromatography was perfluoropropylene oxide. Molecular weight by mass spectrum effusion method is 165 and by vapor density is 164 (calcd. 166). The F^{19} n.m.r. spectrum is consistent with the epoxide structure (see Figure 1). The infrared spectrum shows strong absorption at 6.45 μ which is indicative of perfluoro olefin epoxides.[5]

Anal. Calcd. for C_3F_6O: F, 68.67. Found: F, 67.10.

Compound C (15%, 0.93 mmole) was collected from the chromatograph and shown to be perfluoroacetyl fluoride by comparison of its infrared and mass spectra with those of an authentic specimen. The −196° condensable fraction contained a total of 2.86 mmoles by *P–V* calculation. Mass spectral analysis showed the following components: SiF_4 (0.27 mmole); COF_2, 8.0% (0.23 mmole); CF_4, 33.6% (0.96 mmole); OF_2, 34.3% (0.98 mmole); CO_2, 9.8% (0.28 mmole); and C_2F_6, 4.9% (0.14 mmole). All compounds were identified by comparison of spectra with those of authentic samples.

Spectra.—Infrared spectra were obtained with a Perkin-Elmer Model 21 spectrophotometer equipped with sodium chloride optics. The F^{19} n.m.r. spectra were taken on carbon tetrachloride solutions with a Varian Associates Model HR-40 spectrometer and values are given in cycles per second (c.p.s.) from external trifluoroacetic acid (TFA).

Gas samples were analyzed routinely on a Consolidated Model 21-620 mass spectrometer. Vapor phase chromatograms were obtained with a Wilkens Model A-90-P instrument modified to use low-temperature columns as well as inject and collect gaseous samples.

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[6] Minnesota Mining and Manufacturing Co. trade name for perfluorochlorocarbon lubricants.

[7] General Electric Corp., Model H100 PFL 38-4 with Pyrex envelope.

[8] Minnesota Mining and Manufacturing Co. trade name for perfluorotributylamine. Column was loaded with 30% w./w. FC-43 on 80–100-mesh Chromosorb P.

Compounds of Phosphorus and Fluorine. I. Reaction of Trialkyl Phosphites with Saturated Chlorofluorocarbons

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This is the first paper of a series in which the synthesis and properties of fluorine-containing organophosphorus compounds is explored. Our initial attempts to prepare such compounds by the reaction of trialkyl phosphites with saturated chlorofluorocarbons, described in the present paper, were discontinued when it became evident that products with C–P bonds were not being formed. Subsequent papers will be concerned with reactions which did form products with C–P bonds and with the chemistry of the resulting compounds.

Trialkyl phosphites usually undergo the Arbuzov reaction[2] when treated with saturated alkyl halides, forming products with C–P bonds. In some cases, however, the alkyl halides suffer dehalogenation or dehydrohalogenation, and no C–P bonds are formed. Dehalogenation appears to be the predominant course when the alkyl halides contain two chlorine, bromine, or iodine atoms on adjacent carbon atoms.[3] Some of the alkyl halides also contained fluorine,[3c,h] but in no case was a fluorine atom removed.

The starting point for this investigation was the discovery of an unexpected reaction between tributyl phosphite and Fluorolube® S, one of a group of chlorotrifluoroethylene polymers characterized by a high degree of chemical stability.[4] These polymers should contain few chlorine atoms on adjacent carbon atoms, as they are stabilized by rigorous fluorination. Their structure should therefore be favorable for the replacement of chlorine by phosphonate in the conventional Arbuzov manner. We found, however, that when Fluorolube S was heated with tributyl phosphite in amounts corresponding to a 1:1 ratio of phosphorus to chlorine, a strongly exothermic reaction set in at about 100°, giving butyl chloride and dibutyl phosphorofluoridate as the only identifiable products. The reaction appeared to have proceeded in the manner shown by eq. 1. No butyl fluoride nor dibutyl phosphorochloridate was detected. Efforts to isolate the unsaturated polymer given in eq. 1 were unsuccessful.

$$F[CF_2CFCl]_nF + n(RO)_3P \longrightarrow F[CF{=}CF]_nF + n(RO)_2P(O)F + nRCl \quad (1)$$

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[2] For a recent review, see R. G. Harvey and E. R. De Sombre, "Topics in Phosphorus Chemistry," Vol. 1, M. Grayson and E. J. Griffith, Ed., John Wiley and Sons, Inc., New York, N. Y., 1964, p. 57.

[3] (a) B. A. Arbuzov and B. P. Lugovkin, *Zh. Obshch. Khim.*, **21**, 99 (1951); (b) G. Kamai, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 923 (1952); (c) H. R. Davis, U. S. Patent 2,742,510 (April 17, 1956); (d) V. S. Abramov and N. A. Il'ina, *Zh. Obshch. Khim.*, **26**, 2014 (1956); (e) V. S. Abramov and S. Pall, *Tr. Kazansk. Khim. Tekhnol. Inst.*, **23**, 105 (1957); *Chem. Abstr.*, **52**, 9949 (1958); (f) V. Mark, *Tetrahedron Letters*, 333 (1961); (g) S. Dershowitz and S. Proskauer, *J. Org. Chem.*, **26**, 3595 (1961); (h) I. L. Knunyants and E. Ya. Pervova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1409 (1962); (i) H. Klug and K. Kuchinka, *Ann.*, **677**, 77 (1964).

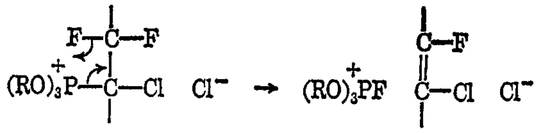
[4] Technical Bulletin No. 30, "Fluorolubes," Hooker Chemical Corp., Niagara Falls, N. Y., 1952.

The undistilled residue from this reaction was a mobile black oil which did not exhibit unsaturation in the infrared. It contained 18% of the phosphorus and 21% of the chlorine introduced with the reagents. The unsaturated polymer, if formed, had apparently undergone further reaction to unidentified products.

To verify the reaction path given in eq. 1, experiments were carried out with model compounds. Tributyl phosphite and 2-chlorononafluorobutane, $CF_3CF_2CFClCF_3$, were found to be unreactive at room temperature, either with or without a solvent. 2,2-Dichlorooctafluorobutane, $CF_3CF_2CCl_2CF_3$, however, reacted so vigorously with tributyl phosphite at room temperature that the reagents could not be simply mixed together. The addition of 0.5 ml. of tributyl phosphite to 0.5 ml. of the chlorofluorocarbon in a test tube produced immediate spattering and fuming. When the tributyl phosphite was added slowly to a solution of the 2,2-dichlorooctafluorobutane in benzene, dibutyl phosphorofluoridate and 2-chloroheptafluoro-2-butene, $CF_3CF{=}CClCF_3$, were produced in 59 and 87% yield, respectively. The 2-chloroheptafluoro-2-butene was a mixture of *cis* and *trans* isomers in about 2:3 ratio. Similar results were obtained with trimethyl phosphite, either in the presence or absence of a solvent. The identification of all three reaction products served to verify the over-all stoichiometry of eq. 1.

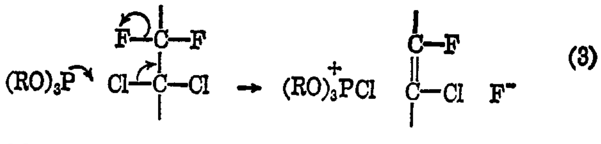
2,2,3-Trichloroheptafluorobutane, $CF_3CFClCCl_2CF_3$, which contains chlorine atoms on adjacent carbon atoms, also gave 2-chloroheptafluoro-2-butene when treated with tributyl phosphite, but in this case the *cis/trans* ratio was about 1:1. The by-products were butyl chloride and dibutyl phosphorochloridate.

Several mechanisms can be considered for reactions of this type, differing both in the position of initial attack and in the subsequent steps. The initial step could be a nucleophilic attack by the phosphite on the carbon atom bearing the chlorine substituent; the resulting quasiphosphonium salt could (a) undergo the Arbuzov reaction, followed by cleavage of the C–P bond, as suggested by Davis,[3c] or (b) decompose *via* the four-center cyclic displacement shown in eq. 2.



(2)

Alternatively, the first step could be a nucleophilic attack by the phosphite on chlorine,[5] giving a different quasiphosphonium salt (eq. 3). Direct attack on



(3)

the chlorine was the basis of Knunyants's mechanism,[3h] which involved a seven-center cyclic displacement, and presumably of other mechanisms which invoked an $(RO)_3PCl_2$ intermediate.[3b,d]

Subsequent breakdown of the quasiphosphonium intermediates of eq. 2 and 3, however, would give different products. The observed products were those of eq. 4, not 5. The results of the present work

$$(RO)_3\overset{+}{P}F\ Cl^- \longrightarrow (RO)_2P(O)F + RCl \quad (4)$$

$$(RO)_3\overset{+}{P}Cl\ F^- \longrightarrow (RO)_2P(O)Cl + RF \quad (5)$$

therefore favor the mechanism given in eq. 2, unless an exchange of chloride for fluoride is postulated. One example appears in the literature of the reaction of a trialkyl phosphite with a perhalocarbon in which different halogen groups were removed, the reaction of triethyl phosphite with 1,2-dichloro-1-iodotrifluoroethane, $CF_2ClCFClI$, but the only product identified was chlorotrifluoroethylene.[3h]

In other experiments, triphenyl phosphite was found to be immiscible with 2,2,3-trichloroheptafluorobutane and Fluorolube S at room temperature. It dissolved in both on heating but separated again on cooling. There was no indication of reaction with the Fluorolube even at 300°. No reaction was observed between 2,2-dichlorooctafluorobutane and dibutyl phosphite or its sodio derivative, nor between 2,2,3-trichloroheptafluorobutane and dibutyl phosphite. In the latter case some hydrogen chloride was evolved, but no 2-chloroheptafluoro-2-butene was detected. No reaction was observed between tributyl phosphite and Du Pont Teflon® polytetrafluoroethylene at temperatures up to the boiling point of the phosphite (240°). Tests for fluoride ion were negative.

Experimental Section

Reagents.—Trimethyl phosphite was prepared from triphenyl phosphite by transesterification.[6] Triphenyl phosphite and Fluorolube® S were Hooker products. Dibutyl phosphite was prepared from tributyl phosphite by treatment with anhydrous hydrogen chloride.[6,7] 2-Chlorononafluorobutane,[8] 2,2-dichlorooctafluorobutane,[9] and 2,2,3-trichloroheptafluorobutane[10] were products of the fluorination of hexachlorobutadiene, on hand from earlier work in these laboratories. The remainder of the reagents and solvents were obtained from commercial sources and used as such, except for the tributyl phosphite which was redistilled.

Spectra.—The infrared spectra were taken on a Beckman IR-4 spectrophotometer. The *cis/trans* ratios in the 2-chloroheptafluoro-2-butenes were estimated by measuring the relative intensities of the *cis* and *trans* bands at 10.1 and 9.9 μ, respectively, using the spectra of the pure isomers given by Sedlak[11] as standards.

Caution: Some of the dialkyl phosphorofluoridates are potent cholinesterase inhibitors. Due regard should be observed for their potentially toxic properties.

Reactions of Trialkyl Phosphites with Chlorofluorocarbons. A. Fluorolube S.—Tributyl phosphite (250 g., 1.0 mole) was added dropwise over a 75-min. period to 116 g. (1.0 g.-atom of Cl) of Fluorolube S under nitrogen at 100°. The butyl chloride which formed was drawn off as required to maintain the reaction temperature at 100°. During the addition the pot contents gradually deepened in color, and at the end were deep red. Distillation gave 168.6 g. (80%) of dibutyl phosphoro-

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[5] Direct attack on halogen in perhaloalkanes by nucleophilic reagents in general was postulated by W. T. Miller, Jr., and R. Becker [Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1963, p. 14M]. For a similar mechanism in which the nucleophile was a trialkyl phosphite, see A. J. Speziale and L. R. Smith, *J. Am. Chem. Soc.*, **84**, 1868 (1962).

[6] C. F. Baranauckas, R. L. K. Carr, and J. J. Hodan, U. S. Patent 3,184,495 (May 18, 1965).

[7] A. N. Pudovik, *Zh. Obshch. Khim.*, **27**, 2755 (1957).

[8] C. I. Gochenour and G. D. Kyker, U. S. Patent 2,436,357 (Feb. 17, 1948); *Chem. Abstr.*, **42**, 5465 (1948).

[9] R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 3005 (1955).

[10] C. F. Baranauckas and W. E. Ashton, U. S. Patent 2,862,036 (Nov. 25, 1958); *Chem. Abstr.*, **53**, 9055 (1959).

[11] J. A. Sedlak, Ph.D. Dissertation, Ohio State University, 1960.

fluoridate in three fractions. The major fraction was redistilled, b.p. 74–76° (1.5 mm.), $n^{25}\mathrm{D}$ 1.3994.

Anal. Calcd. for $C_8H_{18}FO_3P$: P, 14.6. Found: P, 13.6.

The product was further identified by comparison of its infrared spectrum with that of an authentic sample (see below). Aniline tests[12] on the distillates were negative. The literature[13] gives b.p. 84–86° (0.8 mm.), $n^{25}\mathrm{D}$ 1.412, $n^{20}\mathrm{D}$ 1.4013. The residue from this distillation was a mobile black oil, 77.0 g., which showed no unsaturation in the infrared.

Anal. Found: P, 7.4; Cl, 10.4.

Distillation of the combined trap contents from all of these operations gave butyl chloride, b.p. 78–80°, $n^{24}\mathrm{D}$ 1.3998, in 50% yield. No butyl fluoride was detected.

A series of experiments in which the ratio of phosphorus to chlorine was reduced from 1:1 to 1:10 gave products with higher chlorine content and lower phosphorus content, but none of them showed unsaturation in the infrared. No reaction was observed between Fluorolube S and tributyl phosphite or trimethyl phosphite in refluxing benzene (80°).

B. **2-Chlorononafluorobutane.**—Tributyl phosphite (25.0 g., 0.1 mole) and 2-chlorononafluorobutane (25.5 g., 0.1 mole) were found to be immiscible at room temperature. After 2 hr. stirring the mixture was distilled, 90% of the 2-chlorononafluorobutane, b.p. 29–30°, being recovered. Another experiment, in which 100 ml. of benzene was added as a solvent, gave a homogeneous solution, but again no sign of reaction was observed.

C. **2,2-Dichlorooctafluorobutane.**—2,2-Dichlorooctafluorobutane (27.1 g., 0.1 mole) was added dropwise to a solution of 25.0 g. (0.1 mole) of tributyl phosphite in 100 ml. of benzene over a 20-min. period at 25–30°. The reaction was strongly exothermic and was controlled by external cooling. When the addition was ended the solution was stirred at room temperature for 45 min. and then tested with 0.1 *N* iodine in benzene for unreacted phosphite. The test was negative. Distillation through a 3-in. column packed with glass helices gave 19.0 g. (87%) of 2-chloroheptafluoro-2-butene, b.p. 33–38°, identified by its infrared spectrum as a mixture of *cis* and *trans* isomers in about 2:3 ratio, and 12.5 g. (59%) of dibutyl phosphorofluoridate, b.p. 85–87° (2 mm.), identified by analysis, by its infrared spectrum which showed a P–F band[14] at 11.4 μ absent in dibutyl phosphorochloridate, and by a negative aniline test.[12]

Anal. Calcd. for $C_8H_{18}FO_3P$: P, 14.6. Found: P, 14.4.

The literature gives b.p. 33–35 or 32.2° for 2-chloroheptafluoro-2-butene.[8,15]

The substitution of trimethyl phosphite for tributyl phosphite in the reaction described above gave products identified by infrared as 2-chloroheptafluoro-2-butene and dimethyl phosphorofluoridate. This reaction could also be run in the absence of a solvent. 2,2-Dichlorooctafluorobutane (27.1 g., 0.1 mole) added to 12.4 g. (0.1 mole) of trimethyl phosphite gave 10.7 g. (50%) of 2-chloroheptafluoro-2-butene, b.p. 32–34° (*cis*:*trans* mixture in about 2:3 ratio), and 9.5 g. (74%) of dimethyl phosphorofluoridate, b.p. 38–44° (10 mm.), identified by analysis, by its infrared spectrum[14] which contained a P–F band at 11.3 μ absent in dimethyl phosphorochloridate and enhanced bands at 5.2 and 5.5 μ, and by a negative aniline test.

Anal. Calcd. for $C_2H_6FO_3P$: P, 24.2. Found: P, 23.0.

The literature[16] gives b.p. 43.5° (14 mm.). The trap contents from this reaction weighed 12.5 g. (calculated for methyl chloride, 5.0 g.). Infrared analysis showed them to be a mixture of methyl chloride and 2-chloroheptafluoro-2-butene.

D. **2,2,3-Trichloroheptafluorobutane.**—A solution of 25.0 g. (0.1 mole) of tributyl phosphite in 100 ml. of benzene was treated dropwise with 28.8 g. (0.1 mole) of 2,2,3-trichloroheptafluorobutane over a 20-min. period at 25–30°. The reaction was strongly exothermic. When the addition was ended the solution was stirred for 15 min. and then tested for unreacted phosphite with 0.1 *N* iodine in benzene. The test was negative. Distillation gave 13.0 g. of a fraction, b.p. 31–53°, which was redistilled through a 4-in. column packed with glass helices to give a center cut, b.p. 34–35°, identified by its infrared spectrum as 2-chloroheptafluoro-2-butene (*cis*:*trans* mixture in about 1:1 ratio). Further distillation, after removal of the benzene and presumably the butyl chloride, gave a fraction, b.p. 122° (7 mm.), $n^{23}\mathrm{D}$ 1.4264, identified by analysis, by its infrared spectrum, and by a strongly positive aniline test[12] as dibutyl phosphorochloridate.

Anal. Calcd. for $C_8H_{18}ClO_3P$: P, 13.5. Found: P, 13.4.

The literature[17] gives b.p. 129–130° (10 mm.), $n^{20}\mathrm{D}$ 1.4306.

Dibutyl Phosphorofluoridate.—Dibutyl phosphorochloridate, b.p. 117–122° (8 mm.), $n^{25}\mathrm{D}$ 1.4297, was prepared in 89% yield by the chlorination of tributyl phosphite in benzene.[18] The conversion of this substance to the fluoridate proved to be unexpectedly difficult. Even after 22 hr. of refluxing with sodium fluoride in toluene a product could not be obtained which was free from chloridate. The conditions described by Bany[13b] were 10 hr. of refluxing with sodium fluoride in benzene. A stronger fluorinating agent was obviously desirable. Cobalt trifluoride was found to be too reactive, producing a blue solution which deposited blue crystals on standing. Antimony trifluoride, however, was found to be suitable. A slurry of 20.0 g. (0.11 mole) of antimony trifluoride in 150 ml. of benzene was distilled until about 50 ml. of distillate was removed, and then, while still hot, treated dropwise with 22.9 g. (0.1 mole) of dibutyl phosphorochloridate over a 20-min. period. The mixture was heated at reflux for 2 hr., cooled, filtered, treated with lead carbonate to remove any residual acidity, and again filtered. Distillation of this product gave 5.7 g. (27%) of a fraction, b.p. 76° (0.9 mm.), $n^{25}\mathrm{D}$ 1.3990, identified by analysis, by its infrared spectrum which contained a P–F band at 11.4 μ, absent in dibutyl phosphorochloridate, and by a negative aniline test, as dibutyl phosphorofluoridate.

Anal. Calcd. for $C_8H_{18}FO_3P$: P, 14.6. Found: P, 14.9.

Comparison of the infrared spectrum of this product with the spectra of the dibutyl phosphorofluoridates obtained from Fluorolube S and 2,2-dichlorooctafluorobutane showed that the same product was obtained from each.

Acknowledgment.—We are indebted to Mr. Leon A. Zengierski for capable technical assistance, and to Dr. Russell L. K. Carr for helpful discussions during the course of this work.

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[12] B. C. Saunders, "Some Aspects of the Chemistry and Toxic Action of Organic Compounds Containing Phosphorus and Fluorine," Cambridge University Press, London, 1957, p. 48. This test was found to be quite useful for detecting traces of chloridates in phosphorofluoridates.

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

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Preparation of Some Cyclopropanes and Stable Sulfoxonium Ylides from Dimethylsulfoxonium Methylide

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The *trans* isomer of 2-phenylcyclopropanecarboxylic acid is an intermediate for the synthesis of *trans*-2-phenylcyclopropylamine,[1] a potent inhibitor of monoamine oxidase used clinically as an antidepressant agent. In the original synthesis of this acid by the reaction of ethyl diazoacetate with styrene followed by hydrolysis of the resulting ester, a mixture of *cis* and *trans* acids is obtained[2] from which the latter isomer

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[1] Tranylcypromine, Parnate®.

[2] A. Burger and W. L. Yost, *J. Am. Chem. Soc.*, **70**, 2198 (1948).