Fluorinated Heterocyclic Derivatives of Sulfur, Selenium, and Phosphorus[1]

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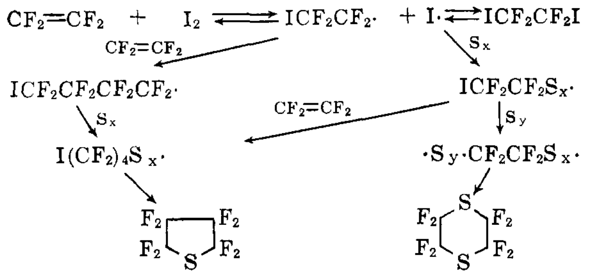
Octafluorothiolane and octafluoro-1,4-dithiane have been obtained directly and in up to 15% and 60% yields, respectively, from reactions of sulfur with tetrafluoroethylene. 2-Trifluoromethylpentafluoro-1,3-dithiolane was usually obtained as a by-product. Similar reactions of tetrafluoroethylene with selenium and phosphorus in the presence of iodine gave octafluoroselenolane, octafluoro-1,4-diselenane, octafluoro-1-iodophospholane, and octafluoro-1,4-diiodo-1,4-diphosphane.

Fluorinated cyclic sulfides with high thermal and chemical stability have now been synthesized from tetrafluoroethylene and sulfur. Fluorinated cyclic selenides and phosphines have been prepared similarly from tetrafluoroethylene and the corresponding elements. Although electrolytic fluorination has been used to prepare perfluorinated cyclic ethers and amines,[2,3] perfluorinated heterocyclic compounds containing only tetra- and hexavalent sulfur have been obtained from cyclic sulfides by this method.[2,4] The literature contains two reports of perfluorinated cyclic sulfides, one produced by heating hexafluoropropylene with sulfur[5] and the other prepared from octafluoro-1,4-diiodobutane and sulfur.[6] No highly fluorinated cyclic selenides or phosphines have been described previously.

Early efforts to interact elemental sulfur and tetrafluoroethylene failed, led to polytetrafluoroethylene, or resulted in explosive decomposition. The use of iodine as a coreactant to activate the tetrafluoroethylene and prevent homopolymerization was, however, successful. Sulfur and and tetrafluoroethylene were found to combine readily in the presence of iodine at 250–300° under pressure to form octafluorothiolane (I) and octafluoro-1,4-dithiane (II) in about 10% and 40% yields, respectively. A high ratio of sulfur to tetrafluoroethylene favored the formation of II almost exclusively as the volatile product. This effect is a result of competition between sulfur and tetrafluoroethylene for the fluorinated free radicals, as indicated in the generalized scheme below.



I II

This scheme is supported by reactions described by Haszeldine and co-workers. They found that sulfur reacts with trifluoromethyl iodide to form bis(trifluoromethyl) disulfide when the temperature is high enough to cause formation of trifluoromethyl radicals by homolytic dissociation of the iodide.[7] Moreover, the diiodide of tetrafluoroethylene is unstable and apparently can decompose by way of a 2-iodotetrafluoroethyl radical when heated.[8] Thus, the diiodide or a mixture of iodine and tetrafluoroethylene could provide a free radical at elevated temeratures capable of attacking sulfur. The recently reported[6] reaction of sulfur with octafluoro-1,4-diiodobutane to form octafluorothiolane in high yield provides direct confirmation of one path in the proposed reaction scheme.

Both I and II are volatile liquids, stable at 300°, resistant to attack by acids, bases, and free radicals, and have high dielectric strength. As a consequence of these properties, conventional combustion techniques give low values in analyses for carbon.

The reaction will also proceed in the presence of a solvent such as carbon disulfide or carbon tetrachloride without the need for iodine as catalyst.[9] At 150–200° and under pressure, use of a solvent allows the preparation of both I and II. Yields are low under these conditions, running about 10–15% for I when an excess of sulfur is avoided. Most solvents interact to some extent to give byproducts, but carbon disulfide has been found to be inert even under extreme conditions of temperature. Thus, sulfur and tetrafluoroethylene react in carbon disulfide for eight to twelve hours at 300° under pressure to form the dithiane II in 50% yield. Formation of the thiolane I can be

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(1) Presented in part at the 140th National Meeting of the American Chemical Society, Chicago, Illinois, September, 1961.

(2) M. Stacey, J. C. Tatlow, and A. G. Sharpe, "Advances in Fluorine Chemistry," Vol. I, Academic Press, Inc., New York, 1960, pp. 139–155.

(3) J. H. Simons, "Fluorine Chemistry," Vol. II, Academic Press, Inc., New York, 1954, p. 340.

(4) F. W. Hoffmann, T. C. Simmons, R. B. Beck, H. V. Holler, T. Katz, R. J. Koshar, E. R. Larsen, J. E. Mulvaney, F. E. Rogers, B. Singleton, and R. S. Sparks, *J. Am. Chem. Soc.*, **79**, 3424 (1957).

(5) H. C. Brown, *J. Org. Chem.*, **22**, 715 (1957).

(6) G. V. D. Tiers, *ibid.*, **26**, 2538 (1961).

(7) G. A. R. Brandt, H. J. Emeleus, and R. N. Haszeldine, *J. Chem. Soc.*, 2198 (1952).

(8) R. N. Haszeldine, *Nature*, **167**, 139 (1951).

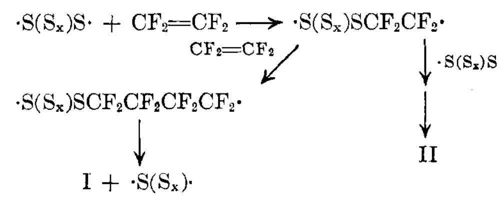
(9) This effect was first observed by Dr. R. T. Stiehl of these laboratories.

minimized in the synthesis of II at 300° by starting with an excess of sulfur.

At temperatures high enough to insure rapid reaction of sulfur with tetrafluoroethylene, neither solvent nor catalyst is necessary. Thus, injection of the fluoroölefin into a pressure vessel containing sulfur heated at 300° led to a 60% yield of octafluorodithiane, whereas attempts to heat the reactants together to 300° gave low yields or explosive reactions.

Since the electrophilic double bond in tetrafluoroethylene should not react readily with a sulfur-sulfur bond, a mechanism based on ionic or very polar intermediates is less likely than one involving free radicals. It is known that the S_8 rings of sulfur rupture on heating to give linear polysulfide chains with radical ends. Detectable amounts of thiyl radicals occur in sulfur at least as low as 190°,[10,11] a lower limit set by the sensitivity of the measurement. Molten sulfur is said to contain S_8 rings and chains in equilibrium up to 159°; above this temperature longer biradical chains of sulfur increase in concentration.[12] These observations correlate with the fact that no reaction of sulfur and tetrafluoroethylene was detected at temperatures much below 150°, even in the presence of a solvent. The carbon disulfide is evidently effective because it provides a phase in which the reactants are mutually soluble, thereby allowing interaction of sulfur and tetrafluoroethylene to compete successfully with cyclodimerization and homopolymerization of tetrafluoroethylene.

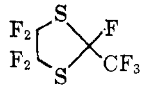
The free radicals present in hot sulfur, then, initiate the reaction by adding to tetrafluoroethylene, just as other free radicals,[13] including thiyl radicals,[14] have been found to add tetrafluoroethylene. The fluorinated radical so formed can then react with more sulfur, ultimately giving the dithiane II, or it can extend the carbon chain by adding to another molecule of tetrafluoroethylene. The latter event leads to a reactive intermediate that can cyclize with loss of sulfur to give the thiolane I.



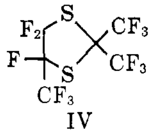
$$\begin{tikzcd}
\cdot S(S_x)S\cdot + CF_2{=}CF_2 \arrow[r] & \cdot S(S_x)SCF_2CF_2\cdot \arrow[dl, "CF_2{=}CF_2"'] \arrow[dd, "\cdot S(S_x)S\cdot"] \\
\cdot S(S_x)SCF_2CF_2CF_2CF_2\cdot \arrow[d] & \\
I + \cdot S(S_x)\cdot & II
\end{tikzcd}$$

The reactions leading to II are a series of condensations with elimination of sulfur that end with monosulfide groups in the product. Since the polysulfides from sulfur and perfluoroalkyl monoiodides degrade thermally to disulfides as the end products,[7,15] elimination of sulfur to form the monosulfide II is probably facilitated by ring formation. There should be little or no strain in large rings containing disulfide bonds,[16] thus it appears that the formation of II is not a result of especially weak sulfur-sulfur bonds in the precursors, but rather a favorable steric arrangement for attack of thiyl radical on carbon to close a ring while sulfur is expelled. The analogous reaction with a fluorinated acyclic disulfide has been accomplished only by irradiation[7]; photochemical cleavage of bis(trifluoromethyl) disulfide led to bis(trifluoromethyl) sulfide and sulfur as final products.

Preparations of II at 300° gave varying amounts of a by-product isomeric with II. This material, which constituted 0–3% of the product boiling around 80°, has been shown to be 2-trifluoromethylpentafluoro-1,3-dithiolane (III). At the high reaction temperature involved, a migration of fluorine can occur during the reaction with concomitant formation of the five-membered dithiolane ring. Separation of II and III was accomplished by vapor phase chromatography, after which III was identified by analysis and nuclear magnetic resonance (n.m.r.). This impurity can most readily be removed from II by treatment with hot base.



III



IV

The presence of trifluoromethyl groups in the fluoroölefin facilitates the fluorine migration. Thus, reaction of sulfur and hexafluoropropylene at 300° gives a product, b.p. 112–113°, that is believed to be 2,2,4-tris(trifluoromethyl)trifluoro-1,3-dithiolane (IV). Although this product has previously been assigned a 1,4-dithiane structure,[5] examination of the relative intensities of the n.m.r. bands for F^{19} show a preponderance of fluorine in trifluoromethyl groups and only minor amounts of difluoromethylene and tertiary fluorine atoms. Furthermore, structure IV can exist only as a racemic mixture, while a mixture of positional as well as stereoisomers would be expected for the dithiane structure. The n.m.r. spectrum gives no indication that the product is a mixture.

Selenium, tetrafluoroethylene, and iodine react to form heterocyclic compounds similar to those obtained from sulfur. Octafluoroselenolane (V) and octafluoro-1,4-diselenane (VI) are formed in low yields when the reaction is conducted at 250°; at higher temperatures the fluorinated cyclic selenides decompose extensively, so that little V

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(10) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, 1957, pp. 334–338.

(11) D. M. Gardner and G. K. Fraenkel, *J. Am. Chem. Soc.*, **78**, 3279 (1956).

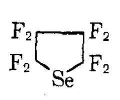
(12) M. Schmidt, *Angew. Chem.*, **73**, 394 (1961).

(13) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, 1957, pp. 250–253.

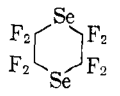
(14) J. F. Harris, Jr., and F. W. Stacey, *J. Am. Chem. Soc.*, **83**, 840 (1961).

(15) M. Hauptschein and A. V. Grosse, *ibid.*, **73**, 5461 (1951).

(16) M. Calvin and J. A. Barltrop, *ibid.*, **74**, 6153 (1952).



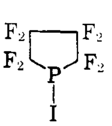
V



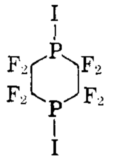
VI

or VI is obtained. These selenides are less stable thermally than the corresponding sulfides, since the latter are unaffected at 300°.[17]

In one experiment, the reaction of red phosphorus with tetrafluoroethylene and iodine showed a tendency to stop at the bis(fluoroalkyl)phosphine stage, iodine atoms satisfying the third valence of phosphorus. Therefore, the major products, octafluoro-1-iodophospholane (VII) and octafluoro-1,4-diiodo-1,4-diphosphane (VIII), are monocyclic compounds.



VII



VIII

VIII is sufficiently stable toward hydrolysis to allow purification by extraction of impurities with cold water. VII dissolves in water with cleavage of one carbon–phosphorus bond, a reaction similar to that reported for iodobis(trifluoromethyl)phosphine.[18] The open chain phosphonous acid obtained by hydrolysis of VII is oxidized by hydrogen peroxide to the phosphonic acid, isolable as the diammonium salt.

$$\mathrm{VII} \xrightarrow{H_2O} H(CF_2)_4P(OH)_2 \xrightarrow{H_2O_2} H(CF_2)_4PO(OH)_2$$

The n.m.r. spectra of the products, together with the analytical data, serve as the basis for identification. From the results obtained by n.m.r., a sulfur, selenium, or phosphorus atom attached to a difluoromethylene group is seen to cause a pronounced chemical shift of the difluoromethylene resonance toward lower field. In the case of VIII, the ring is fixed in a puckered configuration. In this puckered form, the fluorine atoms bonded to the same carbon atom are non-equivalent because of lack of a plane of symmetry through the ring. Therefore, the eight fluorine atoms are distributed into two non-equivalent sets of four atoms each. Two doublets centered around +837 c.p.s. and +1112 c.p.s. arise from one of these sets, and another two doublets centered around +1710 c.p.s. and +1990 c.p.s. arise from the other non-equivalent set. Secondary splitting into doublets arises from $P^{31}-F^{19}$ interactions, and the inequality of coupling (54 c.p.s. for one set and 128 c.p.s. for the other) is a result of two different F—C—P bond angles in the nonplanar ring. This pattern did not collapse to two lines when the spectrum was taken at 100°, indicating a high barrier to axial-equatorial inversion.

Experimental[19]

Octafluorothiolane (I).—A mixture of 8.0 g. (0.25 g.-atom) of sulfur, 24 g. (0.24 mole) of tetrafluoroethylene, and 20 ml. of carbon tetrachloride was heated in an 80-ml. shaker tube at 150° for 6 hr. under autogenous pressure. Distillation of the reaction mixture afforded 4.3 g. (15% yield based on tetrafluoroethylene) of octafluorothiolane, b.p. 42–43°, n^{25}D 1.3050. The n.m.r. spectrum for F^{19} showed bands of equal intensity at +786 c.p.s. for CF_2—S and at +2575 c.p.s. for the other CF_2 group.

Anal. Calcd. for C_4F_8S: F, 65.49; S, 13.82; mol. wt., 232. Found: F, 65.75; S, 13.58; mol. wt., 232 (mass spec.).

Octafluoro-1,4-dithiane (II).—A mixture of 64 g. (2.0 g.-atom) of sulfur and 50 ml. of carbon disulfide was heated at 300° in a 400-ml. shaker tube while 100 g. (1.0 mole) of tetrafluoroethylene was injected continuously over a 2-hr. period. The reaction mixture was then heated at 300° for an additional 12 hr. Distillation gave a fraction, b.p. 45–81°, from which the dithiane was crystallized by cooling at −80°. The product, isolated by filtration, was stirred with aqueous ammonia for 12 hr., dried, and distilled to give 67.4 g. (51% yield based on tetrafluoroethylene) of octafluoro-1,4-dithiane, b.p. 80–81°. A highly purified sample[20] had b.p. 81.5°; m.p. −6.6°; n^{25}D 1.3581. Infrared spectroscopy showed no bands of high frequency such as those associated with multiple bonds. N.m.r. revealed one resonance for F^{19} at +937 c.p.s.

Anal. Calcd. for $C_4F_8S_2$: F, 57.54; S, 24.27; mol. wt., 264. Found: F, 57.50; S, 24.33; mol. wt., 264 (mass spec.).

Octafluorodithiane remains unchanged on being heated in a sealed tube at 200° for several weeks in the presence of metals such as aluminum, copper, or iron and is stable for shorter periods at 300°. It is not affected by prolonged refluxing with fuming nitric acid or with concentrated ammonium hydroxide. In addition it has a low order of toxicity toward mice.

Iodine-Catalyzed Synthesis of Octafluorothiolane and Octafluoro-1,4-dithiane.[21] A.—A mixture of 16.0 g. (0.50 g.-atom) of sulfur, 50.8 g.(0.20 mole) of iodine, and 93 g. (0.93 mole) of tetrafluoroethylene was heated in a 400-ml. shaker tube lined with stainless steel at 150° for 0.5 hr. and then at 300° for 8 hr. The liquid portion of the reaction mixture was distilled to give volatile fractions boiling at 38–43° and 79–83°. Treatment of the lower boiling fraction with mercury to remove free iodine followed by redistillation gave 9.0 g. (8% yield based on tetrafluoroethylene) of octafluorothiolane, b.p. 41–42°. Identification was made by comparison of the n.m.r. spectrum with that of a known sample.

A similar purification of the other fraction gave 27 g. (22% yield based on tetrafluoroethylene) of octafluoro-1,4-

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[17] H. J. Emeleus and R. N. Haszeldine, *Science*, **117**, 314 (1953), report similar low stability for trifluoromethyl derivatives of selenium as compared to those of sulfur.

[18] F. W. Bennett, H. J. Emeleus, and R. N. Haszeldine, *J. Chem. Soc.*, 3598 (1954).

[19] Melting and boiling points are uncorrected. N.m.r. spectra were obtained by means of a high-resolution n.m.r. spectrometer and associated electromagnet, both manufactured by Varian Associates, operating at 40 Mc./sec. and approximately 10,000 gauss. Spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the F^{19} resonance of 1,1,2,2-tetrachloro-1,2-difluoroethane. Negative frequency displacements are for resonances occurring at lower field than the internal reference.

[20] Dr. W. D. Nicoll of these laboratories has found that the main impurity, 2-trifluoromethylpentafluoro-1,3-dithiolane, is preferentially removed on heating at 120° with sodium methoxide. In successive preparations, this dithiolane was present in 0–3% concentration.

[21] C. G. Krespan, U.S. Patent 2,931,803 (1960).

dithiane, b.p. 80–81°, identified by n.m.r. The presence of an impurity was indicated by the low refractive index, n^{25}D 1.3568.

B. A mixture of 16.0 g. (0.50 g.-atom) of sulfur, 50.8 g. (0.20 mole) of iodine, and 30 g. (0.30 mole) of tetrafluoroethylene was heated to 300° in a 400-ml. pressure vessel. Another 19 g. (0.19 mole) of tetrafluoroethylene was injected, and the vessel was then heated for 14 hr. at 300°. Distillation of the liquid product gave mainly octafluoro-1,4-dithiane, along with less than 1 g. of octafluorothiolane. Purification of the main product by stirring it with mercury and then with aqueous ammonia followed by a distillation afforded 25 g. (39% yield based on tetrafluoroethylene) of octafluoro-1,4-dithiane, b.p. 80–81°.

Direct Reaction of Tetrafluoroethylene with Hot Sulfur.—The preparation of octafluoro-1,4-dithiane can be accomplished without the use of solvent or iodine by injection of tetrafluoroethylene into the reactor containing sulfur at 300°. This procedure has given consistently good results, whereas attempts to heat sulfur and tetrafluoroethylene together to high temperatures in a pressure vessel have generally led to explosive reactions or excessive loss of tetrafluoroethylene by cyclodimerization to octafluorocyclobutane.

A 240-ml. shaker tube containing 27.5 g. (0.86 g.-atom) of sulfur was heated at 300° under autogenous pressure while 86 g. (0.86 mole) of tetrafluoroethylene was injected in portions over a 1-hr. period. Heating was continued for an additional 10 hr. at 300°. Distillation gave 61.2 g. (61% yield) of octafluoro-1,4-dithiane, b.p. 79–81°, identified by its n.m.r. spectrum. Octafluorodithiane prepared without carbon disulfide contained 0–1% of the isomeric 2-trifluoromethylpentafluoro-1,3-dithiolane, as determined by gas chromatography (*vide infra*).

2-Trifluoromethylpentafluoro-1,3-dithiolane (III).—Depending on reaction conditions, up to about 3% of 2-trifluoromethylpentafluoro-1,3-dithiolane has been obtained as coproduct with octafluoro-1,4-dithiane. The dithiolane has been isolated from octafluoro-1,4-dithiane by vapor phase chromatography. On a 1/4 in. × 12-ft. silicone oil-on-firebrick column at room temperature the peaks were at 59 and 65 min. for dithiolane and dithiane, respectively. The dithiolane has b.p. 77°, m.p. −83°, n^{25}D 1.3492.

Anal. Calcd. for $C_4F_8S_2$: C, 18.19; F, 57.54; S, 24.27. Found: C, 18.06; F, 57.80; S, 24.28.

The gross n.m.r. spectrum for F^{19} showed a peak for CF_3 centered at +552 c.p.s., a w-s-s-w grouping for CF_2 at +756, +963, +1009, and +1226 c.p.s., and a resonance for CF at +1885 c.p.s. The intensity ratios for the three groups were close to 3:4:1. Additional splitting was apparent in all the peaks, but they were not resolved further.

2,2,4-Tris(trifluoromethyl)trifluoro-1,3-dithiolane (IV).—Reaction of 128 g. (4.0 g.-atoms) of sulfur and 150 g. (1.0 mole) of hexafluoropropylene was carried out at 300° for 36 hr. in a 500-ml. shaker tube. The product, isolated and purified as described by Brown,[5] was 23.1 g. (13% yield based on hexafluoropropylene) of colorless oil, b.p. 112–113°. This material was established by Brown to be $C_6F_{12}S_2$, for which he proposed a 1,4-dithiane structure.

The expected CF_3, CF_2, and CF peaks are shown by n.m.r. spectroscopy to be present, but the F^{19} spectrum is clean and has these peaks in relative intensities of about 10:2:1. This result indicates that fluorine migration has occurred to give 2,2,4-tris(trifluoromethyl)trifluoro-1,3-dithiolane rather than a mixture of bis(trifluoromethyl)-1,4-dithianes. N.m.r. bands occurred at +112 c.p.s. for CF_3, at +95 (hidden), +310, +868, and +1083 c.p.s. (wssw) for CF_2, and at +2580 c.p.s. for CF. Fine structure was evident in each peak.

Octafluoroselenolane (V) and Octafluoro-1,4-diselenane (VI).—An 80-ml. shaker tube charged with 7.9 g. (0.10 g.-atom) of selenium, 12.7 g. (0.05 mole) of iodine, and 25 g. (0.25 mole) of tetrafluoroethylene was heated at 250° under autogenous pressure for 7 hr. From the dark reaction mixture there was obtained by treatment with mercury and distillation 2.7 g. (10% yield based on selenium) of octafluoroselenolane, b.p. 62–63°. N.m.r. bands of equal intensity were found at +727 c.p.s. for CF_2—Se and at +2595 c.p.s. for the other CF_2 group.

Anal. Calcd. for C_4F_8Se: F, 54.48; Se, 28.3. Found: F, 53.92; Se, 27.5, 30.7 (X-ray emission).

A fraction boiling at 107–110° was treated with ether and magnesium to remove tetrafluoroethylene diiodide, and redistillation gave 0.9 g. (5% yield based on selenium) of octafluoro-1,4-diselenane, b.p. 108°. This product was identified only by a positive qualitative test for selenium and a demonstration that the n.m.r. spectrum contained only one peak in a region compatible with CF_2—Se.

Octafluoro-1-iodophospholane (VII) and Octafluoro-1,4-diiodo-1,4-diphosphane (VIII).—A mixture of 7.8 g. (0.25 g.-atom) of red phosphorus, 25.4 g. (0.10 mole) of iodine, and 51 g. (0.51 mole) of tetrafluoromethylene was heated in an 80-ml. pressure vessel at 220° for 8 hr. From the reaction mixture there was obtained by distillation 3.0 g. (4% yield based on iodine) of liquid, b.p. 116–119°, indicated to be impure octafluoro-1-iodophospholane by n.m.r.

The residue from the distillation was sublimed at 50–60° (1 mm.), and the resulting sublimate was extracted with cold water and dried under reduced pressure. In this way there was obtained 14.0 g. (27% yield based on iodine) of octafluoro-1,4-diiodo-1,4-diphosphane as pale yellow crystals, m.p. 73–75.5°. An analytical sample was prepared by recrystallization from petroleum ether. The assigned structure was supported by n.m.r. (see Discussion).

Anal. Calcd. for $C_4F_8I_2P_2$: F, 29.47; I, 49.21; P, 12.01. Found: F, 29.26; I, 49.28; P, 12.03.

Proof of Structure for Octafluoro-1-iodophospholane.—The crude distillate of octafluoro-1-iodophospholane (above) was hydrolyzed by treatment with an excess of cold distilled water. The colorless aqueous solution was evaporated in a stream of air until a second phase appeared, cooled to 0°, and treated with 10 ml. of 12% hydrogen peroxide. Filtration of the brown solution to remove a precipitate of free iodine and then evaporation in a stream of air gave a colorless oil, identified as ω-H-octafluorobutanephosphonic acid by n.m.r. The diammonium salt was prepared by addition of an excess of ammonium hydroxide and removal of water under reduced pressure.

Anal. Calcd. for $C_4H_9F_8N_2O_3P \cdot H_2O$: F, 45.49; N, 8.39; P, 9.27. Found: F, 45.66; N, 8.60; P, 9.26.

Acknowledgment.—Appreciation is due to Dr. H. Foster, Dr. W. D. Phillips, and Mr. C. B. Matthews for calibration and interpretation of the n.m.r. spectra.