67. *The Heptafluoropropyliodophosphines and their Derivatives.*

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Reaction of heptafluoroiodopropane with phosphorus at 200—220° gave bisheptafluoropropyliodophosphine and heptafluoropropyldi-iodophosphine. No trisheptafluoropropylphosphine was found. The two iodo-compounds afforded various derivatives and were less readily hydrolysed than their trifluoromethyl analogues. Heptafluoropropylphosphonous, heptafluoropropylphosphonic, and bisheptafluoropropylphosphinic acid were prepared: all were strong acids. Preliminary experiments on the reaction of heptafluoroiodopropane with arsenic are also described.

Trifluoromethyl compounds of phosphorus are readily prepared by interaction of trifluoroiodomethane and phosphorus at 195—250°.[1] The products, tristrifluoromethylphosphine, iodobistrifluoromethylphosphine, and di-iodotrifluoromethylphosphine, are formed at 230° in the rough proportions 7 : 2 : 1, and increasing temperature favours formation of the tris-compound. The iodine in the two iodo-compounds may readily be replaced by other groups and hydrolysis yields trifluoromethylphosphonous acid,[2] which

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[1] Bennett, Emeléus, and Haszeldine, *J.*, **1953**, 1565.

[2] *Idem, J.*, **1954**, 3598.

can be oxidised to the corresponding phosphonic acid. In the experiments described below the analogous reaction of heptafluoroiodopropane with phosphorus has been studied, to determine the influence of the larger heptafluoropropyl group on the initial reaction and on the properties of a number of derivatives of the products.

Reaction of heptafluoropropyliodopropane with phosphorus began at about 200° and was conveniently carried out at 220—230°. Surprisingly, no trisheptafluoropropylphosphine was isolated but only a mixture of bisheptafluoropropyliodophosphine and heptafluoropropyldi-iodophosphine. This result was obtained even when the conditions should, by analogy with the behaviour of trifluoroiodomethane, have favoured production of the tris-compound. Vapour-phase chromatography was used in attempts to detect the presence of the trisheptafluoropropyl compound.

Tripropylphosphine may be made from the trichloride by the Grignard reaction [3] and the same method has been used for butylphosphines.[4] Trisheptafluoropropylphosphine may, therefore, be accessible by reaction of phosphorus trichloride with heptafluoropropyllithium [5] or heptafluoropropylmagnesium iodide.[6]

Preliminary experiments on the reaction of heptafluoroiodopropane with arsenic showed that, although reaction occurs readily at 200—220° with formation of heptafluoropropyl arsenicals, fluorocarbons are formed simultaneously and prevent the separation and characterisation of the desired products. These fluorocarbons are probably the result of the breakdown of the arsenicals, rather than of decomposition of heptafluoroiodopropane, since they are formed to only a minor extent in the reaction of heptafluoroiodopropane with sulphur at 300—400°.[7] Tristrifluoromethylarsine and trispentafluoroethylarsine decompose at a conveniently measurable rate at 350—410° and 270—310°, respectively,[8] and it is therefore likely that the heptafluoropropyl derivatives would show incipient instability at 200—300°, which, if it led to liberation of radicals such as C_3F_7, would produce fluorocarbons.

The two heptafluoropropyliodophosphines reacted readily with silver chloride to form the corresponding chloro-compounds. Chlorobisheptafluoropropylphosphine added chlorine and formed trichlorobisheptafluoropropylphosphorane, $(C_3F_7)_2PCl_3$, which decomposed at 125° to a complex mixture which included chloroheptafluoropropane, dichloroheptafluoropropylphosphine, and chlorobisheptafluoropropylphosphine. The chief difference between the heptafluoropropyl compounds and their trifluoromethyl analogues, apart from volatility, was in the slower hydrolysis of the former. For example, ethyl bisheptafluoropropylphosphinite was incompletely decomposed by water, even at 150°, whereas the corresponding trifluoromethyl compound, prepared by the interaction of chlorobistrifluoromethylphosphine with alcohol, was hydrolysed at room temperature with quantitative liberation of fluoroform. Similarly, aminobisheptafluoropropylphosphine was only partially hydrolysed at room temperature, whereas aminobistrifluoromethylphosphine was readily decomposed.[9]

Chlorobisheptafluoropropylphosphine also reacted with ammonia to form aminobisheptafluoropropylphosphine, $(C_3F_7)_2P{\cdot}NH_2$ and with ethyl alcohol to form ethyl bisheptafluoropropylphosphinite, $(C_3F_7)_2P{\cdot}OEt$. Alkaline hydrolysis of these compounds resulted in quantitative liberation of heptafluoropropane. Both heptafluoropropyliodo-compounds gave heptafluoropropylphosphonous acid, $C_3F_7{\cdot}PO{\cdot}OH$, with water with elimination of one molecule of heptafluoropropane in the case of the monoiodo-compound. The acid was isolated in a pure state (b. p. 71°/0·7 mm.) by hydrolysis of dichloroheptafluoropropylphosphine. The titration curve showed it to be a strong and monobasic acid. It

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[3] Davies, Pearse, and Jones, *J.*, 1929, 1262.
[4] Davies and Jones, *J.*, 1929, 33.
[5] Pierce, McBee, and Judd, *J. Amer. Chem. Soc.*, 1954, **76**, 474.
[6] McBee, Pierce, and Meiners, *ibid.*, 1953, **75**, 2516.
[7] Haszeldine and Kidd, *J.*, 1955, 3871.
[8] Ayscough and Emeléus, *J.*, 1954, 3381.
[9] Harris, *J.*, 1958, 512.

was oxidised in aqueous solution by iodine and also reduced mercuric to mercurous chloride at 60°. When the aqueous solution was oxidised by hydrogen peroxide, heptafluoropropylphosphonic acid was formed. This was isolated as white deliquescent needles of the dihydrate. The titration curve was similar to that of trifluoromethylphosphonic acid, the slightness of the first inflection indicating a small ratio of the two dissociation constants, as is found for oxalic and malonic acids. Mean values of the dissociation constants calculated by Britton's method[10] were $1{\cdot}3 \times 10^{-1}$ and $1{\cdot}1 \times 10^{-4}$, the corresponding values of pK_1 and pK_2 being 0·9 and 3·96. Heptafluoropropylphosphonic acid was stable to hydrolysis by excess of alkali. Bisheptafluoropropylphosphinic acid was prepared from trichlorobisheptafluoropropylphosphorane by adding the stoicheiometric amount of water. It was a white deliquescent solid, the titration curve of which was typical of a strong, monobasic acid. At room temperature excess of sodium hydroxide liberated 1 mol. of heptafluoropropane. The acid sublimed without decomposition in a vacuum at 66—68°.

When the conductivities of the two monobasic acids were measured in water at 25° the plots of equivalent conductivity against the square root of molar concentration were linear at low concentrations, extrapolation to zero concentration giving values of the equivalent conductivities at infinite dilution of 367 ohm^{-1} cm.^{2} for $(C_3F_7)_2PO{\cdot}OH$ and 363 ohm^{-1} cm.^{2} for $C_3F_7{\cdot}PHO{\cdot}OH$.[11] The derived equivalent conductivities of the bisheptafluoropropylphosphinate and heptafluoropropylphosphonite ions are 17·5 ± 1·5 and 12·9 ± 1·5 ohm^{-1} cm.^{2}. For heptafluoropropylphosphonic acid the plot of equivalent conductivity against square root of concentration is not a straight line. The same is true of trifluoromethylphosphonic acid,[12] as well as sulphuric,[13] malonic, and oxalic acid. For none of these acids can the equivalent conductivity at infinite dilution be determined. A rough comparison between the acidity of these heptafluoropropyl oxyacids of phosphorus and the acidity of sulphuric and perchloric acids was made with a limited range of Hammett indicators.[14] It was shown that the acidity of saturated solutions of bisheptafluoropropylphosphinic and heptafluoropropylphosphonic acid, and of liquid heptafluoropropylphosphonous acid (H_0 = approx. -6 to -8) was appreciably greater than that of 70% perchloric acid (H_0 = approx. $-5{\cdot}5$) but less than that of 98% sulphuric acid (H_0 = approx. -9). These high acidities are associated with the presence in the molecule of the electronegative heptafluoropropyl group. It is not possible, however, to decide from the data whether these acids are stronger or weaker than their trifluoromethyl analogues.

The ultraviolet absorption spectra of the heptafluoropropyliodophosphines and their derivatives show the same general features as those of the trifluoromethyl derivatives, with the expected small shift of the absorption maxima to longer wavelengths.[15] The infrared spectra show the pattern of C–F stretching frequencies and CF_3 and CF_2 angle deformation frequencies which seem to be characteristic of all compounds containing the n-C_3F_7 group.[16] The detailed shape of the absorption pattern between 1000 and 1350 cm.$^{-1}$ allows compounds with one C_3F_7 group to be distinguished from those with two C_3F_7 groups. The spectrum of aminobisheptafluoropropylphosphine shows N–H stretching frequencies at 3480 and 3390 cm.$^{-1}$, and the NH_2 angle deformation frequency at 1567 cm.$^{-1}$. In the spectra of ethyl bistrifluoromethylphosphinite and ethyl bisheptafluoropropylphosphinite, C–H stretching frequencies appear between 2860 and 3000 cm.$^{-1}$, and the frequencies characteristic of the OEt system between 1360 and 1500 cm.$^{-1}$. The frequencies at 1039 and 937 cm.$^{-1}$ in the spectrum of $(CF_3)_2P{\cdot}OEt$ and at 1026 and 945 cm.$^{-1}$ in the spectrum of $(C_3F_7)_2P{\cdot}OEt$ are assigned to the P–O–Et group and in each case the first frequency is

[10] Britton, " Hydrogen Ions," Chapman and Hall, 1955, Vol. I, p. 218.
[11] For data *see* J. D. Smith, Ph.D. Thesis, Cambridge, 1958.
[12] Emeléus, Haszeldine, and Paul, *J.*, 1955, 563.
[13] Sherrill and Noyes, *J. Amer. Chem. Soc.*, 1926, **48**, 1861.
[14] Long and Paul, *Chem. Rev.*, 1957, **57**, 1.
[15] Haszeldine, *J.*, 1953, 1764.
[16] Hauptschein and Grosse, *J. Amer. Chem. Soc.*, 1951, **73**, 2461.

within the narrow range (1050—980 cm.$^{-1}$) for characteristic P–O–Et absorption. The spectra of the heptafluoropropylphosphorus oxyacid derivatives are similar to those of the trifluoromethyl compounds and have been useful for characterising these materials.

EXPERIMENTAL

Preparation of Heptafluoroiodopropane.—Heptafluoroiodopropane (b. p. 40—41°) was made in 90% yield by heating dry silver heptafluorobutyrate with iodine.[16] The product decomposed slowly in light, forming iodine and perfluorohexane.

Reaction of Heptafluoroiodopropane with Red Phosphorus.—Red phosphorus was washed with sodium hydroxide solution and water and dried (P_2O_5). Purified phosphorus (25 g.) was placed in a 300 ml. stainless-steel autoclave, heptafluoroiodopropane (*ca.* 50 g.) was introduced *in vacuo* and the autoclave was filled with dry nitrogen before being sealed. In 8 hr., little reaction occurred at 200°, but at 220—230° about 60% of the heptafluoroiodopropane was converted into phosphorus derivatives. These were pumped from the autoclave *in vacuo* and condensed at $-46°$. They contained about 70% of bisheptafluoropropyliodophosphine, the balance being heptafluoropropyldi-iodophosphine. The proportion of the latter increased with the reaction time at 235°. *Bisheptafluoropropyliodophosphine* and *heptafluoropropyldi-iodophosphine* were separated with difficulty by trap-to-trap fractional condensation: the former condensed at $-23°$ (Found: C, 14·9; C_3F_7, 67·7; I, 25·5. $C_6F_{14}IP$ requires C, 14·5; C_3F_7, 68·1; I, 25·6%) and the latter at $-3°$ (Found: C, 8·1; C_3F_7, 35·0; I, 54·8; P, 6·6. $C_3F_7I_2P$ requires C, 7·9; C_3F_7, 37·2; I, 55·9; P, 6·8%). The former was a pale yellow liquid, the vapour pressure of which (at 0—80°) was given by $\log_{10} p(\text{mm.}) = 8{\cdot}096 - 2170/T$. The extrapolated b. p. was 135°, the latent heat of evaporation 9920 cal./mole, Trouton's constant 23·7, and the m. p. $-108°$. Only slight decomposition and disproportionation occurred during the vapour-pressure measurements, which were made with a spiral pressure gauge used as a null instrument. The compound reacted with mercury, giving a colourless liquid, probably tetrakisheptafluoropropyldiphosphine. The monoiodo-compound was rapidly and quantitatively decomposed by aqueous alkali, all the fluorine being liberated as heptafluoropropane. This reaction was used in analysis. Bisheptfluoropropyliodophosphine (0·329 g., 0·663 mmole) and water (4 ml.), when sealed in a Carius tube for 4 days, gave heptafluoropropane (0·112 g., 0·660 mmole) (Found: *M*, 169. Calc. for C_3HF_7: *M*, 170). When the remaining volatile material was heated at 100° for 48 hr. a further 0·0997 g. (0·592 mmole) of heptafluoropropane was formed, equivalent to almost complete decomposition of the heptafluoropropylphosphonous acid formed in the aqueous hydrolysis at room temperature. Hydrolysis by 2N-hydrochloric acid gave a similar result, half of the heptafluoropropane being liberated at room temperature and half at 120°.

Heptafluorodi-iodopropylphosphine was a yellow liquid, the vapour pressure of which (at 40—120°) was given by $\log_{10} p(\text{mm.}) = 7{\cdot}350 - 2070/T$. The extrapolated b. p. was 190° ± 2°, the latent heat of evaporation 9470 cal./mole, Trouton's constant 20·5, and the m. p. $-18°$. There was appreciable decomposition during the vapour-pressure determination at the higher temperatures. The compound was decomposed by aqueous alkali, and all of the fluorine was liberated as heptafluoropropane.

No trisheptafluoropropylphosphine was isolated even after reaction at 300°, which favours formation of tristrifluoromethylphosphine from trifluoroiodomethane and phosphorus. Then the product from the autoclave reaction (3·46 g.) was treated with silver chloride to convert the two iodo-compounds into chloro-derivatives, and next with α-naphthylamine (1 g.) in pentane, and there was no volatile product. Since both chloro-compounds react with α-naphthylamine and, by analogy with tristrifluoromethylphosphine, the trisheptafluoropropyl compound would not, this experiment strongly supports the absence of the latter.

Since the two iodotrifluoromethylphosphines are known to disproportionate to products which include tristrifluoromethylphosphine, the disproportionation of the heptafluoroiodophosphines was studied with a Perkin–Elmer vapour-phase fractometer. Purified bisheptafluoropropyliodophosphine and heptafluoropropyldi-iodophosphine, when passed through the column, had retention times of 2·3—2·5 and 13·3—13·8 min. That of heptafluoroiodopropane was 1·1—1·2 min. By estimating the areas under the peaks in the record it was shown that a pure sample of the monoiodo-compound when heated at 220° in a Carius tube (48 hr.) gave unchanged material (75%), di-iodo-compound (2%), and heptafluoroiodopropane (16%). The di-iodo-compound when heated similarly gave unchanged material (18%), monoiodo-compound

(36%), and heptafluoroiodopropane (46%). Phosphorus tri-iodide was also produced in the disproportionation but was not introduced into the column. In neither case was there a peak attributable to trisheptafluoropropylphosphine. Bennett *et al.*[1] showed that a considerable amount of tristrifluoromethylphosphine was formed on disproportionation under similar conditions.

Derivatives of the Heptafluoropropyliodophosphines.—(a) *Chlorobisheptafluoropropylphosphine.* Bisheptafluoropropyliodophosphine (11·6 g.), sealed in a Carius tube with silver chloride (35 g.) for 11 days, gave *chlorobisheptafluoropropylphosphine* (8·95 g., 96%) (Found: C, 17·7; Cl, 8·6; C_3F_7, 83·2; P, 7·5%; *M*, 397. $C_6ClF_{14}P$ requires C, 17·8; Cl, 8·8; C_3F_7, 83·5; P, 7·7%; *M*, 404). It was a colourless liquid; vapour pressures (at 10—100°) were given by $\log_{10} p(\text{mm.}) = 7{\cdot}883 - 1956/T$. The b. p. was 118—119°, the latent heat of evaporation 8970 cal./mole, Trouton's constant 22·9, and the m. p. −75°. Hydrolysis by excess of 20% sodium hydroxide solution was rapid and quantitative at room temperature. Chlorobisheptafluoropropylphosphine (0·270 g., 0·669 mmole), sealed with water (4 ml.) for 4 days at 20°, gave heptafluoropropane (0·114 g., 0·672 mmole) (Found: *M*, 168. Calc. for C_3HF_7: *M*, 170).

(b) *Dichloroheptafluoropropylphosphine.* Heptafluoropropyldi-iodophosphine (4·09 g.), similarly treated with silver chloride, gave *dichloroheptafluoropropylphosphine* (2·39 g., 98%) (Found: Cl, 26·0; C_3F_7, 62·7; P, 11·9%; *M*, 272. $C_3Cl_2F_7P$ requires Cl, 26·2; C_3F_7, 62·5; P, 11·4%; *M*, 271). Vapour pressures (at 0—75°) were given by $\log_{10} p(\text{mm.}) = 7{\cdot}744 - 1748/T$. The b. p. was 86·4° ± 1°, the latent heat of evaporation 8000 cal./mole, Trouton's constant 22·3, and the m. p. −90°. This and the preceding compound disproportionated less readily than the iodo-analogues.

(c) *Trichlorobisheptafluoropropylphosphorane.* Chlorobisheptafluoropropylphosphine (8·38 g., 20·7 mmoles) and chlorine (1·47 g., 20·7 mmoles) were sealed in a Carius tube and allowed to warm slowly from −78° to room temperature. The volatile product was *trichlorobisheptafluoropropylphosphorane* (9·54 g., 97%) (Found: Cl, 22·1. $C_6Cl_3F_{14}P$ requires Cl, 22·2%). The vapour pressure (at 50—120°) was given by $\log_{10} p(\text{mm.}) = 7{\cdot}46 - 2094/T$. The b. p. was 184° ± 2°, the latent heat of evaporation 9580 cal./mole, and Trouton's constant 20·8. There was slow decomposition at 125° in 16 hr.: chloroheptafluoropropane, identified by its infrared spectrum, dichloroheptafluoropropylphosphine, and chlorobisheptafluoropropylphosphine (0·108 g.) were produced. Hydrolysis of trichlorobisheptafluoropropylphosphorane (0·218 g., 0·458 mmole) with excess of 20% sodium hydroxide solution at room temperature (48 hr.) gave heptafluoropropane (0·0778 g., 0·458 mmole) and, when the alkaline hydrolysate was evaporated to dryness, the infrared spectrum of the residue indicated the presence of disodium heptafluoropropylphosphonate. Aqueous hydrolysis of trichlorobisheptafluoropropylphosphorane gave no heptafluoropropane.

(d) *Aminobisheptafluoropropylphosphine.* Chlorobisheptafluoropropylphosphine (2·23 g., 5·5 mmoles) and sodium-dried ammonia (0·189 g., 11·1 mmoles) were condensed together at −46° and allowed to warm to room temperature. The product on fractionation gave *aminobisheptafluoropropylphosphine* (2·082 g., 98%) (Found: C, 17·9; H, 0·5; N, 4·3; NH_2 as NH_3, 4·0; C_3F_7, 88·4. $C_6H_2F_{14}NP$ requires C, 18·7; H, 0·5; N, 3·6; NH_2, 4·15; C_3F_7, 87·8%). The product was a colourless liquid. The vapour pressure (at 20—120°) was given by $\log_{10} p(\text{mm.}) = 7{\cdot}743 - 2022/T$. The b. p. was 143° ± 1°, the latent heat of evaporation 9250 cal./mole, Trouton's constant 22·2, and the m. p. −23°. The compound (0·306 g., 0·794 mmole) was hydrolysed slowly by 15% sodium hydroxide solution and gave heptafluoropropane (0·272 g., 1·59 mmoles). A second sample (0·147 g., 0·383 mmole) was sealed with 2N-hydrochloric acid (5 ml.) for three weeks and gave heptafluoropropane (0·0645 g., 0·379 mmole) and 0·376 mmole of ammonia in the hydrolysate. Hydrolysis by water at room temperature was very slow but at 100° the amine (0·449 g., 1·165 mmoles) gave in 48 hr. 0·263 g. (1·545 mmoles) of heptafluoropropane, indicating partial hydrolysis of the ammonium bisheptafluoropropylphosphinite formed in the first stage. The presence of this salt was confirmed by the infrared spectrum of the solid left on freeze-drying of the aqueous hydrolysate.

(e) *Ethyl bisheptafluoropropylphosphinite.* Chlorobisheptafluoropropylphosphine (3·73 g., 9·23 mmoles) and ethanol (0·432 g., 9·21 mmoles), when shaken at room temperature, gave *ethyl bisheptafluoropropylphosphinite* (3·55 g., 93%) (Found: C, 21·5; H, 1·8; C_3F_7, 81·4; P, 8·0. $C_8H_5F_{14}OP$ requires C, 23·2; H, 1·2; C_3F_7, 81·6; P, 7·5%). The vapour pressure (at 30—120°) was given by $\log_{10} p(\text{mm.}) = 8{\cdot}17 - 2190/T$. The b. p. was 140—141°, the latent heat 10,020 cal./mole, Trouton's constant 24·3, and the m. p. −47°. Hydrolysis of the compound by

20% alkali at 20° was incomplete in 12 hr., even with shaking, but was quantitative after several days. When ethyl bisheptafluoropropylphosphinite (0·158 g., 0·383 mmole) was shaken with water for 5 days only 0·004 g. of heptafluoropropane was liberated. When the products were resealed and heated at 150° for 24 hr. a further 0·0105 g. (0·062 mmole) of heptafluoropropane was formed. The compound was apparently immiscible with water and, after heating, two layers were still present. *Ethyl bistrifluoromethylphosphinite* was prepared similarly from chlorobistrifluoromethylphosphine[1] (Found: C, 22·8; H, 2·5; CF_3, 64·7; P, 15·6%; *M*, 214. $C_4H_5F_6OP$ requires C, 22·5; H, 2·3; CF_3, 64·5; P, 14·5%; *M*, 214). The vapour pressure (at $-25°$ to 55°) was given by $\log_{10} p(\text{mm.}) = 7{\cdot}890 - 1739/T$. The b. p. was 74° ± 1°, the latent heat 7960 cal./mole, and Trouton's constant 22·9. The compound was decomposed rapidly and completely by 20% aqueous sodium hydroxide at 20°. A sample (0·136 g., 0·668 mmole), when sealed for 1 week with water at 20°, gave 0·0485 g. (0·695 mmole) of trifluoromethane. When the tube was resealed and heated at 120° for 12 hr. a further 0·0450 g. (0·642 mmole) of trifluoromethane was evolved.

Preparation of Heptafluoropropylphosphonous Acid.—Dichloroheptafluoropropylphosphine (1·9 g., 7·0 mmoles) was added to water (0·252 g., 14·0 mmoles) and gave a clear liquid without evolution of heptafluoropropane. When distilled through a column this gave *heptafluoropropylphosphonous acid* (1·18 g., 72%) (Found: C_3F_7, 71·4; P, 13·4%; equiv., 230. $C_3H_2F_7O_2P$ requires C_3F_7, 72·2; P, 13·3%; equiv., 234). The titration curve was characteristic of a strong monobasic acid with complete neutralisation at pH 7—8. Heptafluoropropylphosphonous acid was decomposed quantitatively to heptafluoropropane by excess of 15% sodium hydroxide solution. There was slow decomposition by water at 100° and heptafluoropropane was again liberated. The acid was slowly but almost quantitatively oxidised by a solution of iodine buffered with sodium hydrogen carbonate. When 20 ml. of solution containing 0·0535 mmole of acid were mixed with 50 ml. of 3% mercuric chloride solution and 50 ml. of 3% glacial acetic acid (5 ml.) there was no precipitate in the cold but, in 12 hr. at 60°, 0·0242 g. (0·0572 mmole) of mercurous chloride was precipitated.

Preparation of Heptafluoropropylphosphonic Acid.—Dichloroheptafluoropropylphosphine (3·43 g.) was added to water (5 ml.) and treated with 50% unstabilised hydrogen peroxide (10 ml.). Freeze-drying gave deliquescent needles of *heptafluoropropylphosphonic acid dihydrate* (3·2 g.) (Found: equiv., 142. $C_3H_6O_5F_7P$ requires equiv., 143). The crystalline *dianilinium salt* was prepared by reaction with excess of aniline in ethanol [Found: C, 41·5; H, 3·5; N, 6·5. $C_3H_7{\cdot}PO(OH)_2,2C_6H_5{\cdot}NH_2$ requires C, 41·3; H, 3·7; N, 6·4%]. Similar reaction with one equivalent of aniline gave the *monoaniline salt* which recrystallised from ethanol [Found: C, 31·8; H, 2·9; N, 4·3. $C_3H_7{\cdot}PO(OH)_2,C_6H_5{\cdot}NH_2$ requires C, 31·5; H, 2·6; N, 4·1%]. Hydrolysis of the dianiline salt (0·614 g.) with an equivalent quantity of 0·25N-sodium hydroxide gave *disodium heptafluoropropylphosphonate* (0·354 g.) [Found: C, 12·2; H, 0·3%; equiv. (by elution on ion-exchange column and titration), 146. $C_3F_7{\cdot}PO(ONa)_2$ requires C, 12·25; H, 0·6%; equiv., 147]. The sodium salt gave no heptafluoropropane in 20% sodium hydroxide solution at 125° during 48 hr.

Preparation of Bisheptafluoropropylphosphinic Acid.—Distilled water was added dropwise to trichlorobisheptafluoropropylphosphorane (9·54 g.). When slightly more than the stoicheiometric amount had been added the product became solid. Volatile products were pumped off, leaving *bisheptafluoropropylphosphinic acid* (6·42 g.) as a deliquescent white solid [Found: equiv., 406. $(CF_7)_2PO{\cdot}OH$ requires equiv., 402]. The titration curve was typical of that for a strong monobasic acid. When 0·163 g. (0·406 mmole) of the acid was sealed with excess of sodium hydroxide solution (2 days) 0·066 g. (0·30 mmole) of heptafluoropropane was evolved. The infrared spectrum of the solid residue from the hydrolysate after evaporation showed the presence of disodium heptafluoropropylphosphonate. The solid acid sublimed undecomposed in a vacuum at 66—68°.

Silver bisheptafluoropropylphosphinate was prepared by adding silver oxide to the acid and recrystallised from ether [Found: C, 13·6; Ag, 20·7. $(C_3F_7)_2PO{\cdot}OAg$ requires C, 14·1; Ag, 21·2%]. Its hydrolysis was similar to that of the free acid. The *aniline salt* was also prepared [Found: C, 29·7; H, 2·1; N, 3·2%; equiv., 490. $(C_3F_7)_2PO{\cdot}OH,C_6H_5{\cdot}NH_2$ requires C, 29·1; H, 1·7; N, 2·8%; equiv., 495].

Reaction of Heptafluoroiodopropane with Arsenic.—In preliminary experiments heptafluoroiodopropane and arsenic were heated in a stainless-steel autoclave (300 ml.) at 200° for 48 hr. The volatile product was a clear yellow liquid, 87% of which distilled at 58—61°/20 mm. There was no sign of separation into fractions and analysis of the distillate by alkaline hydrolysis gave: C_3F_7, 49·5; As, 10·0; I, 15·4% (Total 74·9%). After hydrolysis, a drop of oil remained which was unattacked by alkali or aqua regia. Its infrared spectrum showed strong absorption at 1450—1000 cm.$^{-1}$, the region of the C–F stretching frequencies. The oil was, therefore, probably fluorocarbon, which could well form azeotopes with the heptafluoropropyl arsenicals. In further experiments the reaction temperature was reduced to minimise fluorocarbon formation, and the volatile products were analysed for C_3F_7, As, and I. At 147°, after 9 hours' heating the yield of arsenicals was 4% and no oil remained on hydrolysis of the volatile reaction product. Heating at 153° gave 10% of fluorocarbon.

The ultraviolet absorption in light petroleum (Pet) and as vapour (V) between 450 and 200 mμ of the halogenoheptafluoropropylphosphines, recorded on a Cary recording spectrophotometer, is tabulated.

Ultraviolet absorption of the halogenoheptafluoropropylphosphines.

		$\lambda_{max.}$	ε	$\lambda_{min.}$	ε
$C_3F_7PI_2$	Pet	270	3700	248	2880
		222	5900	213	5820
$(C_3F_7)_2PI$	Pet	286	1100	253	710
	V	287	1400	250	570
		220	2700	211	2400
$C_3F_7PCl_2$	Pet	223—233	600	—	—
	V	223—230	740		
$(C_3F_7)_2PCl$	Pet	233	270	221	200

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