317. *Organometallic and Organometalloidal Fluorine Compounds. Part VII.*[*] *Trifluoromethyl Compounds of Phosphorus.*[†]

By F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine.

The interaction of phosphorus and trifluoroiodomethane at 200—220° yields tristrifluoromethylphosphine, $P(CF_3)_3$, iodobistrifluoromethylphosphine, $P(CF_3)_2I$, di-iodotrifluoromethylphosphine, $P(CF_3)I_2$, and phosphorus iodides. The trifluoromethyl compounds are quantitatively hydrolysed to fluoroform by dilute sodium hydroxide solution. Their conversion into $(CF_3)_3PCl_2$, $(CF_3)_2PCl$, $(CF_3)_2P{\cdot}CN$, $CF_3{\cdot}PCl_2$, and $(CF_3)_2P{\cdot}P(CF_3)_2$ is described. The iodo-compounds disproportionate when heated. Comparisons are made with the methyl analogues, and ultra-violet and infra-red spectra are presented and discussed.

The methods commonly used for the preparation of alkyl derivatives of phosphorus cannot readily be applied to the preparation of the corresponding perfluoroalkyl derivatives, but the direct interaction of white phosphorus and a perfluoroalkyl iodide such as trifluoroiodomethane has proved successful. This reaction, which is believed to involve radical intermediates, can be carried out in sealed Pyrex tubes or in stainless-steel autoclaves, and, in the optimum temperature range of 200—220°, yields tristrifluoromethylphosphine, iodobistrifluoromethylphosphine, di-iodotrifluoromethylphosphine, tetraiododiphosphine, and phosphorus tri-iodide. At the higher temperature over 80% of the product other than trifluoroiodomethane consists of tristrifluoromethylphosphine; below 200° the reaction is slow, but produces a higher percentage yield of the iodo-compounds which, because of the reactivity of the iodine atoms, are of greater chemical interest. Somewhat increased yields of the iodotrifluoromethylphosphines may be obtained by use of red phosphorus instead of white, but the most convenient method is to heat white phosphorus and trifluoroiodomethane at the optimum temperature, remove the iodo-compound by a rough fractionation *in vacuo,* and recycle the tristrifluoromethylphosphine and unchanged trifluoroiodomethane. The use of a mixture of phosphorus and phosphorus tri-iodide also increases the proportion of iodobistrifluoromethylphosphine in the complex equilibria:

$$(CF_3)_3P \rightleftharpoons (CF_3)_2PI \rightleftharpoons CF_3{\cdot}PI_2 \rightleftharpoons CF_3I + P$$

Hexafluoroethane is not formed, nor are quaternary phosphonium compounds isolated (cf. ethyl iodide and phosphorus: Carius, *Annalen*, 1866, **137**, 117; Crafts and Silva, *J.*, 1871, 629; Masson and Kirkland, *J.*, 1889, 135; methyl iodide: Auger, *Compt. rend.*, 1904, **139**, 639, 671). The excess of white phosphorus used in the reaction is converted into red phosphorus, a change known to be catalysed by iodine. Reaction of excess of phosphorus with trifluoroiodomethane above 250° gives phosphorus tri- and pentafluoride and hexafluoroethane as major products.

The iodotrifluoromethylphosphines disproportionate when heated, and the equilibria indicated above can also be set up by heating tristrifluoromethylphosphine with iodine:

$$\begin{aligned} 2(CF_3)_2PI &\rightleftharpoons (CF_3)_3P + CF_3{\cdot}PI_2 \\ 2CF_3{\cdot}PI_2 &\rightleftharpoons (CF_3)_2PI + PI_3 \\ (CF_3)_3P + I_2 &\rightleftharpoons (CF_3)_2PI + CF_3I \end{aligned}$$

The arsenic analogues show similar behaviour (Part V, *J.*, 1952, 2552).

Tristrifluoromethylphosphine is a colourless, spontaneously inflammable liquid which boils (17°) some 20° below its methyl analogue (b. p. 37·8°; Rosenbaum and Sandberg, *J. Amer. Chem. Soc.*, 1940, **62**, 1622) [cf. $As(CF_3)_3$, b. p. 33·3°, and $AsMe_3$, b. p. 49·5°, Part VI, *loc. cit.*]. The chlorine analogue of tristrifluoromethylphosphine is unknown, but Hoffman (*J. Amer. Chem. Soc.*, 1930, **52**, 2995) reports b. p. 100°/7 mm. for $P(CH_2Cl)_3$. Compounds comparable in molecular weight to tristrifluoromethylphosphine are triphenyl-

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[*] Part VI, preceding paper.

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phosphine (b. p. >360° ; Michaelis, *Annalen*, 1885, **229**, 295) and tributylphosphine (b. p. 150°/50 mm. ; Davies and Jones, *J.*, 1929, 33).

Tristrifluoromethylphosphine is markedly different from trialkylphosphines by virtue of its strongly electronegative trifluoromethyl groups. The unsubstituted alkylphosphines (*e.g.*, PMe_3) are characterised by compound formation with carbon disulphide, sulphur, silver iodide, and other metallic salts, but introduction of fluorine into the molecule prevents, or at least appreciably inhibits, such compound formation. No reaction could be detected between tristrifluoromethylphosphine and sulphur or carbon disulphide at temperatures up to 200°. Triarylphosphines similarly do not react with carbon disulphide although they react smoothly with sulphur. The trifluoromethyl group acts like a pseudo-halogen in this connection, since phosphorus trichloride reacts with sulphur only at 140°, and no carbon disulphide addition compound has been reported; and phosphorus trifluoride fails to react with sulphur even at 440° (Moissan, " Le Fluor et ses Composés," Steinheil, Paris, 1900, p. 160).

Chlorine reacts violently with trialkylphosphines with attack on the alkyl groups, to give a mixture of chloroalkyl phosphines, but tristrifluoromethylphosphine at −40° smoothly gives tristrifluoromethylphosphorus dichloride in almost quantitative yield. The methyl analogue of the quinquevalent phosphorus compound (Me_3PCl_2) has not been described, although the phenyl analogue has been obtained by a reaction at −80° (Jensen, *Z. anorg. Chem.*, 1943, **250**, 257). Tristrifluoromethylphosphorus dichloride can be distilled without decomposition at 370 mm., but explodes violently near the b. p. at 760 mm. (*ca.* 94°).

Tristrifluoromethylphosphine and iodine react only at >100°, and no intermediate addition compound, $(CF_3)_3PI_2$, has been detected; iodotrifluoromethylphosphines, trifluoroiodomethane, and phosphorus tri-iodide are formed.

Iodobistrifluoromethylphosphine and di-iodotrifluoromethyl phosphine are liquids (b. p. 73° and 69°/29 mm. respectively), which liberate iodine on exposure to light. The former is rapidly oxidised in air. Like tristrifluoromethylphosphine they are rapidly and quantitatively hydrolysed by dilute aqueous alkali, and the trifluoromethyl groups are liberated as fluoroform ; the arsenic compounds behave similarly (Part V, *loc. cit.*). Unlike the iodo-trifluoromethyl arsenicals and tristrifluoromethylphosphine, the iodotrifluoromethylphosphines are rapidly decomposed by water at room temperature. One molecular proportion of fluoroform is liberated from iodobistrifluoromethylphosphine, whereas no fluoroform is obtained from the di-iodo-compound. In the latter case, evaporation of the hydrolysis product *in vacuo* yields a white, hygroscopic, crystalline, strong, dibasic acid, which shows reducing properties. The constitution of this acid, which on oxidation yields a second strong, dibasic acid, $CF_3{\cdot}PO(OH)_2$, is being studied in greater detail.

The iodine atoms in iodobistrifluoromethyl- and di-iodotrifluoromethyl-phosphine are reactive and may be replaced by other halogens or pseudo-halogens. Thus, with silver chloride almost quantitative yields of chlorobistrifluoromethylphosphine and dichlorotrifluoromethylphosphine are obtained, and with silver cyanide the mono-iodo-compound yields cyanobistrifluoromethylphosphine :

$$(CF_3)_2PI \xrightarrow{AgX} (CF_3)_2PX ; \quad CF_3{\cdot}PI_2 \xrightarrow{AgX} CF_3{\cdot}PX_2$$

These volatile compounds are readily hydrolysed by aqueous alkali with quantitative evolution of fluoroform, but unlike the parent iodo-compounds do not react with mercury at room temperature.

Iodobistrifluoromethylphosphine reacts with mercury at room temperature to give tetrakistrifluoromethyldiphosphine, a stable, colourless liquid, b. p. 84° :

$$2(CF_3)_2PI + Hg \longrightarrow (CF_3)_2P{\cdot}P(CF_3)_2 + HgI_2$$

Iodobistrifluoromethylarsine reacts similarly with mercury, but whereas cacodyl, the methyl analogue of the arsenic compound, is well known, the preparation of the methyl derivative of diphosphine has not been definitely established. Attachment of the strongly electronegative fluoroalkyl groups to metalloidal atoms M (= P, As, Sb, S, Se) thus stabilises the M–M bond. The linking of two phosphorus atoms by the reaction described above is novel in phosphorus chemistry, and few compounds containing the P–P bond are known. The existence of tetraphenyldiphosphine (b. p. 400°) seems established (Köhler and Michaelis, *Ber.*, 1877, **10**, 807) but few of its reactions have been reported. Halogen derivatives of diphosphine are known (P_2Cl_4, P_2I_4; Besson and Fournier, *Compt. rend.*, 1910, **150**, 102; Gay-Lussac, *Ann. Chim. Phys.*, 1814, **91**, 9; Doughty, *J. Amer. Chem. Soc.*, 1905, **27**, 1444; Germann and Traxler, *ibid.*, 1927, **49**, 307), and also diphosphine itself (Gattermann and Haussknecht, *Ber.*, 1890, **23**, 1174), and it would be expected that P_2F_4 should also exist.

The constitution of tetrakistrifluoromethyldiphosphine has been established by its reaction with iodine at 280°, four mols. of trifluoroiodomethane being obtained; bromine similarly yields four mols. of bromotrifluoromethane. Treatment of tetrakistrifluoromethyldiphosphine with aqueous alkali liberates only part of the fluorine as fluoroform, the remainder forming fluoride and bistrifluoromethylphosphinous acid. It is believed that hydrolysis occurs by attack on the P–P bond :

$$(CF_3)_2P{\cdot}P(CF_3)_2 \longrightarrow (CF_3)_2PH + (CF_3)_2P{\cdot}OH$$

and a detailed quantitative study in support of this mechanism will be reported in a later paper.

Tristrifluoromethylphosphine shows only end absorption in the ultra-violet. Step-wise replacement of the trifluoromethyl groups by iodine produces the expected shifts to the red, as shown in Table 1. The figures show that solvent shifts are small. The corresponding data for the arsenic compounds (Part VI, *loc. cit.*), summarised in Table 2 (light petroleum solutions), show that the spectra are very similar but with a bathochromic shift on changing from phosphorus to arsenic. This effect is also shown by comparison of tristrifluoromethyl-phosphine and -arsine (Table 3). The marked chromophoric effect of the P–P bond is shown by the spectrum of tetrakistrifluoromethyldiphosphine ($\lambda_{max.}$ 216 mμ; ε *ca.* 4000) [cf. $(CF_3)_2As{\cdot}As(CF_3)_2$, $\lambda_{max.}$ 223; ε 3000; Part VI].

TABLE 1.

	Solvent	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$	$\lambda_{infl.}$	ε
$(CF_3)_2PI$	Light petroleum	282	900	246	280	—	—
	Ether	279	1,000	248	500	—	—
	Vapour	278	1,200	241	400	—	—
CF_3PI_2	Ether	266	5,900	246	4000	320	2600
	Light petroleum	267	3,800	244	2300	320	1400
PI_3	Ether	360	8,800	324	5840	—	—
		291	14,500	248	2000	—	—

TABLE 2.

	$\lambda_{max.}$	$\varepsilon_{max.}$		$\lambda_{max.}$	$\varepsilon_{max.}$
$(CF_3)_2AsI$	290	1200	AsI_3	378	1,600
CF_3AsI_2	271	4200		280	5,600
	229	6500		225	12,000
	$\lambda_{infl.}$ 325 (ε, 1700)				

TABLE 3.

$(CF_3)_3P$	λ	250	240	230	220
	ε	—	—	2·1	11·7
$(CF_3)_3As$	ε	1·89	6·75	12·6	18·7

The infra-red spectra of certain trifluoromethylphosphorus derivatives are recorded in the Experimental, and are useful for identifications. The carbon–fluorine stretching vibrations lie in the 8—9-μ region, showing two main maxima for compounds $CF_3{\cdot}PX_2$ (X = Cl, I); compounds $(CF_3)_2PX$ (X = I, CN) show three main maxima, and $(CF_3)_3P$ has four maxima in this region. Like the arsenic compounds (Part VI), the phosphorus compounds show a strong band at *ca.* 13·3 μ [$CF_3{\cdot}PI_2$ 13·5; $(CF_3)_2PI$ 13·4; $(CF_3)_2P{\cdot}P(CF_3)_2$ 13·37; $(CF_3)_2P{\cdot}CN$, $(CF_3)_2PCl$, $CF_3{\cdot}PCl_2$ 13·3; $(CF_3)_3P$ 13·25 μ], which is probably a CF_3 deformation frequency rather than a C–P stretching vibration. Daasch and Smith (*Ind. Eng.*

Chem., 1951, **23**, 853) have attributed bands in this region to C–P stretching vibrations in certain compounds, and their data suggest that, if correctly assigned, the vibration moves to shorter wave-length with increase in negativity of the groups attached to phosphorus [PMe_3, 14·1, 15·3; $Et{\cdot}PCl_2$, 13·2, 13·8; $CCl_3{\cdot}PO(OEt)_2$, 13·0, 13·5]. Overtones of the C–F vibrations are apparent at *ca.* 4·4 μ, and for cyanobistrifluoromethylphosphine the sharp absorption band at 4·56 μ is the C≡N stretching vibration.

EXPERIMENTAL

General Technique.—The phosphorus compounds were manipulated in absence of air in a vacuum-system where practicable. Reactions were carried out in Pyrex tubes (30—50 ml.), sealed *in vacuo* with careful exclusion of air and moisture, or in stainless-steel autoclaves (100 or 300 ml.); reaction products were transferred *in vacuo*, and purified by fractional condensation or by distillation through a short column in an atmosphere of nitrogen. B. p.s were determined by distillation or by an isoteniscope, and molecular weights by Regnault's method.

Analysis.—Many of the compounds prepared were rapidly and quantitatively hydrolysed to fluoroform and phosphite by treatment with 10% aqueous hydroxide (10 ml.); the reaction is fast, but at least 24 hr. were allowed to ensure its completion. Fluoroform was measured in the vacuum-system, and the aqueous phase was analysed for halogen (when present), or was oxidised with nitric acid, and phosphorus determined as phosphomolybdate. Ionic fluorine was determined by titration with thorium nitrate, and covalent fluorine by sodium fusion followed by steam-distillation of the acidified solution and titration with thorium nitrate.

Note. The use of sodium peroxide instead of sodium for fusion causes violent explosions.

Preparation of Trifluoroiodomethane.—The preparation from silver trifluoroacetate (Haszeldine, *J.*, 1951, 584) was adapted to a large scale : silver trifluoroacetate (1 mole) and powdered iodine (1·6 moles) were mixed in a 4-l. flask, and reaction was initiated by heating a small section of the flask with a free flame. Heating was controlled to give a steady evolution of gas which was passed up a tower down which 10% aqueous sodium hydroxide was running. After drying over phosphoric anhydride the crude trifluoroiodomethane was purified in the vacuum-system (0·9 mole).

The method of *J.*, 1948, 2188 was used in the earlier experiments.

Reaction of Phosphorus with Trifluoroiodomethane.—Commercial stick phosphorus was purified by dipping it into carbon disulphide until the outer oxide layer became detached, and was transferred in a carbon dioxide atmosphere to the reaction vessel and dried *in vacuo.* In a typical early experiment, trifluoroiodomethane (2·94 g.) was sealed *in vacuo* in a Carius tube containing purified phosphorus (3 g.). There was no reaction after 24 hr. at 100°, but after 48 hr. at 220° the tube contained a red solid and a liquid less volatile than trifluoroiodomethane. Fractionation gave unchanged trifluoroiodomethane (30%), *tristrifluoromethylphosphine* (0·7 g., 84%) [Found : C, 14·2; CF_3 (as CHF_3), 86·4; P, 13·5%; *M*, 238. C_3F_9P requires C, 15·1; CF_3, 86·9; P, 13·1%; *M*, 238], *iodobistrifluoromethylphosphine* (0·3 g., 15%), b. p. 72—73°, n_D^{15} 1·403 [Found : C, 8·6; CF_3 (as CHF_3) 46·9; I, 42·5; P, 10·4%; *M*, 297. C_2F_6IP requires C, 8·1; CF_3, 46·9; I, 42·8; P, 10·5%; *M*, 296], and *di-iodotrifluoromethylphosphine* (0·05 g., 1%), b. p. 69°/29 mm., n_D^{20} 1·630 [Found : CF_3 (as CHF_3) 16·6; I, 72·7; P, 8·1. CF_3I_2P requires CF_3, 16·7; I, 71·8; P, 8·8%]. Yields are based on trifluoroiodomethane used, and for the two iodo-compounds are values from bulked products from a number of tubes of the above type. Phosphorus iodides were detected qualitatively in the involatile red solid residue.

Red phosphorus (3 g.), purified by washing with 10% aqueous sodium hydroxide, water, and ethanol and dried *in vacuo*, was similarly heated at 260° for 48 hr. with trifluoroiodomethane (3·8 g.), to give tristrifluoromethylphosphine (0·85 g., 54%) (*M*, 237), iodobistrifluoromethylphosphine (0·71 g., 24%) (*M*, 295), di-iodotrifluoromethylphosphine (0·05 g., 1%), and trifluoroiodomethane (0·226 g., 6%) (*M*, 196).

Results obtained for the reaction of trifluoroiodomethane (50 g.) with white phosphorus (50 g.) in a 300-ml. autoclave are shown in the annexed table (yields based on CF_3I used).

Temp.	$P(CF_3)_3$	$P(CF_3)_2I$	$P(CF_3)I_2$	CF_3I recovered
195°	0·5 g., 25%	2 g., 32%	6 g., 42%	*ca.* 85%
210	1·5 g., 47%	1·5 g., 21%	4 g., 28%	*ca.* 85%
230	7·1 g., 70%	3·7 g., 20%	2·7 g., 6%	50%

Optimum yields of iodo-compounds were obtained by heating trifluoroiodomethane (70 g.) with phosphorus (50 g.) at 195—200° for 48 hr., separating the iodo-compounds in the product by a rough vacuum-fractionation, and recycling the tristrifluoromethylphosphine and unchanged trifluoroiodomethane without addition of fresh phosphorus to the autoclave until *ca.* 10 g. of the fluoro-iodide remained (3 times). The products were tristrifluoromethylphosphine (3·2 g., 12%), iodobistrifluoromethylphosphine (12 g., 23%), di-iodotrifluoromethylphosphine (48 g., 37%), and trifluoroiodomethane (14·5 g., 21%). Improved yields of the iodo-compounds were also obtained by heating phosphorus (50 g.), iodine (50 g.), and trifluoroiodomethane (60 g.) to 200° for 48 hr., removing the iodo-compounds and recycling three times as above : tristrifluoromethylphosphine (3·14 g., 13%), iodobistrifluoromethylphosphine (8·65 g., 19%), di-iodotrifluoromethylphosphine (19·2 g., 18%), and trifluoroiodomethane (29 g., 49%).

A large excess of phosphorus (*e.g.*, 150 g. instead of 50 g.) favours formation of phosphorus trifluoride and hexafluoroethane.

Properties and Reactions of Tristrifluoromethylphosphine.—The compound is a liquid which solidifies to a glass when cooled in liquid nitrogen. It can be heated in glass to 200° without decomposition, is insoluble in, denser than, and stable to, air-free water at room temperature, and inflames in air. The vapour pressure, determined by standard techniques over the range $-25°$ to 12°, is expressed by the formula $\log_{10} p$ (mm.) $= 7{\cdot}323 - 1289{\cdot}6/T$, whence the b. p. is 17·3° ± 0·1°, the latent heat of vapourisation 5890 cal./mole, and Trouton's constant 20·3.

No compound formation could be detected when tristrifluoromethylphosphine was heated to 180° for 3 days with sulphur; no change was apparent after the phosphine had been heated with carbon disulphide at 120° for 8 hr., and two layers were still present on cooling. Compound formation could not be detected when silver iodide, or a solution of silver iodide in aqueous potassium iodide, was shaken with tristrifluoromethylphosphine at room temperature, and the phosphine was recovered quantitatively. Mercuric iodide also failed to combine with tristrifluoromethyl phosphine at room temperature. The possibility of compound formation with salts of the platinum metals has not been investigated.

Tristrifluoromethylphosphine (0·188 g.) was recovered unchanged after being heated with water (10 ml.) for 16 hr. at 100°. After 12 hr. at 200°, fluoroform (0·077 g.) was isolated and characterised, representing 46% hydrolysis of the phosphine. The compound was more stable to N-hydrochloric acid, since 99% was recovered after 24 hr. at 180°.

Tristrifluoromethylphosphine (0·392 g.) was condensed in a Pyrex tube containing sodium hydroxide (1 g.) and water (15 ml.), to give an immediate reaction at 20°. After 48 hr. the volatile products yielded fluoroform (0·338 g., 98%) (Found : *M*, 70. Calc. for CHF_3 : *M*, 70), identified tensimetrically.

No reaction was detected between iodine (1 g.) and tristrifluoromethylphosphine (0·971 g.) after 12 hr. at 100°, but at 180° crystals of phosphorus tri-iodide were deposited and after 24 hr.' fractionation gave trifluoroiodomethane (0·788 g., 34%) (*M*, 196), iodobistrifluoromethylphosphine (0·262 g., 16%) (*M*, 295), di-iodotrifluoromethylphosphine (0·162 g., 4%), and recovered tristrifluoromethylphosphine (0·419 g., 43%) (*M*, 239). A small amount of fluoroform (0·026 g.) was also present, arising from reaction with traces of moisture retained by iodine even when dried over phosphoric oxide *in vacuo* for 7 days.

Tristrifluoromethylphosphine (2·08 g.) reacted with chlorine (0·575 g.) in a sealed tube at $-45°$. After 4 hr. the tube was cooled to $-63°$, and the excess of chlorine removed by pumping to leave a white solid, which was distilled at reduced pressure under nitrogen, to give *tristrifluoromethylphosphorus dichloride* (1·50 g., 56%), b. p. 71°/368 mm., m. p. 20·5° [Found : Cl, 22·9 (Volhard); F, 55·2. $C_3Cl_2F_9P$ requires Cl, 23·0; F, 55·3%]. Attempts to distil the compound at 760 mm. brought about explosive decomposition.

Reactions of Iodobistrifluoromethylphosphine.—The compound is a colourless liquid which attacks mercury, fumes in air, has a pungent smell, and is spontaneously inflammable only in an excess of air. It is best stored at low temperature in the dark, since it liberates iodine on exposure to light.

When the compound (0·517 g.) was heated to 205° for 48 hr. in a sealed 40-ml. tube, disproportionation occurred to give tristrifluoromethylphosphine (0·124 g., 45%) (*M*, 235), iodobistrifluoromethylphosphine (0·242 g., 47%) (*M*, 294), di-iodotrifluoromethylphosphine (0·025 g., 2%), and traces of hexafluoroethane (0·02 g., 8%) and trifluoroiodomethane (0·005 g., 2%), together with characteristic red-orange, prismatic crystals of phosphorus tri-iodide.

Alkaline hydrolysis of iodobistrifluoromethylphosphine (0·188 g.) with 10% aqueous sodium hydroxide (15 ml.) at 20° for 24 hr. gave fluoroform (0·0885 g., 99%) (*M*, 70), and the hydrolysate yielded silver iodide (0·146 g., 98%).

The iodo-compound (0·182 g.) formed a lower layer when sealed with distilled water (10 ml.), but rapidly dissolved, with liberation of gas from the aqueous phase. After 5 days at 20°, the only volatile product was fluoroform (0·0427 g., 50%). Further experiments gave values of 50 ± 2%. The iodine had been liberated quantitatively as iodide (Found: I, 42·5. Calc. for C_2IF_6P: I, 42·9%).

When the reaction tube was resealed and heated at 100° for 12 hr., a further quantity (0·026 g., 32%) of fluoroform (*M*, 71) was obtained.

The reaction of iodobistrifluoromethylphosphine (0·537 g.) with mineral acid (15 ml. of N-hydrochloric acid) follows a similar course. The immediate reaction soon subsided and after 4 days' fractionation gave fluoroform (0·120 g., 47%) (*M*, 71); by resealing, and heating at 100° for 16 hr., a further quantity of fluoroform (0·125 g., 49%) (*M*, 70) was obtained.

Iodobistrifluoromethylphosphine (0·669 g.), sealed with silver cyanide (0·521 g.) at 20° for 24 hr., gave silver iodide (0·541 g.) and *cyanobistrifluoromethylphosphine* (0·411 g., 95%), b. p. 48°, n_D^{20} 1·3248 [Found: CF_3 (as CHF_3), 70·0; CN, 13·3%; *M*, 195. C_3NF_6P requires CF_3, 70·7; CN, 13·3%; *M*, 195], as a colourless liquid with a spontaneously inflammable vapour.

The iodo-phosphine (0·925 g.) was similarly treated with silver chloride (1·184 g.), to give *chlorobistrifluoromethylphosphine* (0·622 g., 97%), b. p. 21° (Found: CF_3, 67·2; Cl, 17·1%; *M*, 204·5. C_2ClF_6P requires CF_3, 67·3; Cl, 17·3%; *M*, 204·5), as a spontaneously inflammable liquid which does not attack mercury. Treatment of chlorobistrifluoromethylphosphine (0·160 g.) with 10% aqueous sodium hydroxide (10 ml.) gave fluoroform (0·109 g., 100%).

Tetrakistrifluoromethyldiphosphine.—Excess of redistilled mercury (6 ml.) was sealed with iodobistrifluoromethylphosphine (7·11 g.) and shaken vigorously for 2 days, to give mercury iodides and *tetrakistrifluoromethyldiphosphine* (3·34 g., 82%), b. p. 83—84° (Found: C, 13·8; F, 65·5%; *M*, 338. $C_4F_{12}P_2$ requires C, 14·2; F, 67·4%; *M*, 338). Analysis of this compound proved difficult, and no method was found for determining phosphorus directly, since sodium fusion gives some phosphide and attempts to oxidise with sodium peroxide gave explosions; alkaline hydrolysis does not liberate all the fluoroform quantitatively. Unchanged iodo-compound cannot be separated easily from tetrakistrifluoromethyldiphosphine, and it is preferred to bring about complete reaction by vigorous shaking, without which the reaction is incomplete after 3 weeks. The product is a colourless liquid, insoluble in and denser than water, with which it does not react at room temperature. The constitution of this inflammable compound was established by reaction with iodine: the diphosphine (0·340 g.) was sealed with an excess of iodine (7 g.) and heated at 280° for 48 hr., to give trifluoroiodomethane (0·751 g., 95%). A similar reaction with bromine gave bromotrifluoromethane (0·342 g., 94%) (*M*, 147), and analysis of the phosphorus bromides obtained gave P, 17·9% (Calc. for $C_4F_{12}P_2$: P, 18·3%). Tetrakistrifluoromethyldiphosphine was recovered unchanged after 24 hr. heating at 210°.

Reactions of Di-iodotrifluoromethylphosphine.—The compound is a yellow, oily liquid which fumes in air, readily attacks mercury, and liberates iodine. It was purified before use by distillation at reduced pressure from red phosphorus: it had b. p. 133°/413 mm., 103°/132 mm., 73°/37 mm., 69°/29 mm.; it decomposes when heated at 760 mm.

Di-iodotrifluoromethylphosphine (0·385 g.), treated with 10% aqueous sodium hydroxide (10 ml.) at 20° for 48 hr., gave fluoroform (99·5%) (*M*, 70), sodium phosphite, and sodium iodide (100%). The di-iodo-compound reacts readily with water without liberation of fluoroform, to give, on evaporation of the aqueous solution *in vacuo*, a white *substance* of empirical formula $CF_3{\cdot}P(OH)_2,H_2O$ [Found: F, 37·2%; *M* (by titration), 152. $CH_4O_3PF_3$ requires F, 37·5%; *M*, 152].

The di-iodo-compound (2·483 g.), heated at 240° for 48 hr., gave trifluoroiodomethane (0·177 g., 13%) (*M*, 195), tristrifluoromethylphosphine (0·130 g., 23%) (*M*, 235), iodobistrifluoromethylphosphine (0·424 g., 41%) (*M*, 292), unchanged di-iodotrifluoromethylphosphine (0·323 g., 13%), and phosphorus tri-iodide.

Interaction of di-iodotrifluoromethylphosphine (0·959 g.) and silver chloride (1 g.) at 20° for 24 hr., then 100° for 30 min., gave *dichlorotrifluoromethylphosphine* (0·379 g., 82%), b. p. 37° (Found: CF_3, 40·1; Cl, 40·8%; *M*, 171. CCl_2F_3P requires CF_3, 40·3; Cl, 41·5%; *M*, 171), as a liquid stable to mercury. Hydrolysis of the dichloro-compound (0·215 g.) with 5% aqueous sodium hydroxide (10 ml.) at 20° for 24 hr. gave fluoroform (0·0875 g., 99·5%) (*M*, 70). The reaction of the compound with water will be described later.

Ultra-violet and Infra-red Spectra.—The ultra-violet spectra were measured on Beckman DU or Unicam instruments, as solutions or as vapours in silica cells [$\varepsilon = 760 \times 22{\cdot}4 \times DT/273\,lp$, where D = optical density, T = temperature (K), l = cell length (cm.), and p = pressure of vapour (mm.)]. A Perkin–Elmer Model 21 Double Beam Instrument with rock-salt optics was employed for the infra-red spectra (annexed).

$(CF_3)_3P$		$(CF_3)_2PI$	$(CF_3)_2P{\cdot}CN$	$(CF_3)_2PCl$	$CF_3{\cdot}PI_2$ *	$CF_3{\cdot}PCl_2$	$(CF_3)_2P{\cdot}P(CF_3)_2$
4·09 (w)	7·64 (m)	4·44 (m)	4·40 (m)	4·32	7·86 (m)	4·39 (m)	4·42 } (m)
4·35 (m)	7·83 (m)	4·51 (m)	4·56 (s)	4·42 } (m)	8·64 (s)	5·28 (w)	4·47
4·46 (m)	8·13 (s)	7·85 (w)	7·84 (m)	4·46	8·75 (s)	7·40 (w)	5·35 (w)
5·06 (w)	8·45 (s)	7·96 (w)	8·23 (s)	5·20 (m)	9·00 (s)	7·55 (w)	7·27 (w)
5·17 (w)	8·67 (s)	8·31 (s)	8·47 (s)	7·25 (m)	9·32 (m)	7·90 (m)	7·67 (m)
5·25 (w)	8·87 (s)	8·45 (m)	8·74 (s)	7·44 (m)	13·55 (s)	8·35 (s)	7·82 (m)
5·32 (w)	9·60 (m)	8·60 (s)	8·88 (s)	7·59 (m)		8·53 (m)	8·39 (s)
5·56 (w)	9·77 (m)	8·84 (s)	9·71 (m)	7·95 (s)		8·70 (s)	8·57 (s)
5·71 (m)	10·03 (m)	8·93 (m)	10·62 (w)	8·10 (m)		8·93 (m)	8·77 (s)
5·95 (w)	10·87 (m)	9·26 (m)	10·84 (m)	8·27 (s)		9·54 (w)	8·95 (s)
6·07 (w)	11·87 (w)	9·73 (m)	11·76 (m)	8·57 (s)		10·4 (w)	9·71 (m)
6·30(w)	12·57 (w)	10·54 (w)	13·24 } (s)	8·85 (s)		12·57 (s)	10·55 (w)
6·70 (w)	13·25 (s)	11·7 (w)	13·34	9·75 (s)		12·82	11·68 (m)
7·19 (m)	13·73 (m)	12·57 (m)	14·05 (m)	10·55 (w)		12·92	12·55 (w)
7·43 (m)		13·34 } (s)		11·03 (w)		12·99 } (m)	13·37 (s)
		13·40		11·47 (w)		13·30	
		14·0 (w)		12·3 (s)		13·34	
				12·93 (w)			
				13·25 } (m)			
				13·33			
				13·95 (m)			

w = weak, m = medium, s = strong. Spectra of vapour unless marked * for capillary film.

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UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, February 5th,* 1953.]