

## The Preparation and Hydrolysis of Tertiary Alkyl(perfluoroalkyl)phosphines

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The phosphines  $R(R_F)_2P$  ( $R_F = CF_3$ ,  $R = Me, Bu^a, Bu^i, Ph$ ;  $R_F = C_3F_7$ ,  $R = Bu^a, Ph$ ) and  $Bu_2^a(CF_3)P$ , and the phosphinous chloride  $Bu(CF_3)PCI$ , have been made from the chlorides  $(R_F)_2PCl$  or  $R_FPCl_2$  and organolithium compounds in ether-hexane at  $-78^\circ$ . The phosphines  $R_2(C_3F_7)P$  ( $R = Et, Ph, CF_3$ ) and  $CF_3(C_3F_7)_2P$  have been made from the compounds  $R_2PCl$  or  $CF_3PCl_2$  and heptafluoropropyl-lithium. The phosphine  $(CF_3)_2(C_3F_7)P$  was oxidised by nitrogen dioxide to the phosphine oxide  $(CF_3)_2(C_3F_7)PO$ , which was hydrolysed by water. Infrared and n.m.r. spectra are discussed. The hydrolyses of the compounds  $R(CF_3)_2P$  with alkali in water-ethanol follow second-order kinetics, and rate constants at  $25^\circ$  decrease in the order  $R = Bu^a > Bu^i > Ph$ .  $CF_3$  was cleaved more easily than  $C_3F_7$  from the unsymmetrical phosphine  $(CF_3)_2(C_3F_7)P$ , but from the phosphine oxide  $(CF_3)_2(C_3F_7)PO$  and from perfluoroalkyl phosphonites and phosphinates, the rate of cleavage of  $CF_3$  was similar to that of  $C_3F_7$ .

UNSYMMETRICAL tertiary phosphines with both alkyl and perfluoroalkyl groups have been made from trifluoriodomethane and tertiary <sup>1-3</sup> or secondary <sup>4</sup> phosphines, from

tristrifluoromethylphosphine and iodomethane,<sup>5</sup> from reactions involving cleavage of phosphorus-phosphorus bonds,<sup>2,6</sup> or from organomercury compounds.<sup>7</sup> From all these methods except the last, the products were isolated

<sup>1</sup> R. N. Haszeldine and B. O. West, *J. Chem. Soc.*, 1956, 3631.

<sup>2</sup> M. A. A. Beg and H. C. Clark, *Canad. J. Chem.*, 1962, **40**, 283.

<sup>3</sup> W. R. Cullen, *Canad. J. Chem.*, 1962, **40**, 426.

<sup>4</sup> A. B. Burg, K. K. Joshi, and J. F. Nixon, *J. Amer. Chem. Soc.*, 1966, **88**, 31.

<sup>5</sup> R. N. Haszeldine and B. O. West, *J. Chem. Soc.*, 1957, 3880.

<sup>6</sup> M. A. A. Beg and H. C. Clark, *Canad. J. Chem.*, 1961, **39**, 564.

<sup>7</sup> R. C. Dobbie and H. J. Emeléus, *J. Chem. Soc. (A)*, 1966, 367.

in low yield after tedious purification. It seemed worthwhile, therefore, to examine the preparation of alkyl-(perfluoroalkyl)phosphines from Grignard or organolithium reagents and phosphorus halides.<sup>8</sup> We chose bisperfluoroalkylphosphinous chlorides for study since these are more volatile and less susceptible to disproportionation than the iodides. After preliminary experiments with Grignard reagents we found that reactions with organolithium compounds were cleaner, and these are discussed in this paper. Preliminary kinetic experiments on alkaline hydrolyses related to the preparative work are also described.

#### EXPERIMENTAL

Materials were manipulated in a vacuum system or in a dry-box filled with nitrogen. Solutions of alkyl-lithiums in hydrocarbon-ether mixtures were prepared from lithium dispersions (100  $\mu$ ) and analysed by standard procedures.<sup>9,10</sup>

materials were separated by trap-to-trap distillation, and the product (2.59 g., 78%) condensed at  $-23^\circ$ . There was no increase in yield when reaction times were increased to 4 hr. With ether-hexane ratios less than 1:1 (v/v), the white precipitate formed more reluctantly and yields were reduced. For example, from the reactants  $(\text{CF}_3)_2\text{PCl}$  (5.14 mmoles) and  $\text{BuLi}$  (5.17 mmoles), in pentane (3 ml.) and ether (0.3 ml., 2.8 mmoles), 2.26 mmoles of the phosphine was isolated (44%).  $\text{Bu}(\text{CF}_3)_2\text{P}$  is a colourless liquid, unreactive towards mercury below  $100^\circ$ , but spontaneously inflammable in air. It freezes to a glass at  $-90$  to  $-100^\circ$ .

A sample of the phosphine (0.120 g., 0.531 mmole) was immiscible and did not react with water in a sealed tube during 48 hr. at  $25^\circ$ , but gave trifluoromethane (0.041 g., 0.59 mmoles, 56% of 2 equiv.) after 48 hr. at  $130^\circ$ . When shaken in a sealed tube with an excess of 10% aqueous potassium hydroxide for 48 hr. at  $25^\circ$ ,  $\text{Bu}(\text{CF}_3)_2\text{P}$  (0.367 mmole) gave trifluoromethane (0.721 mmole), showing that both trifluoromethyl groups were cleaved from the phosphine under these conditions. In a tube containing

TABLE I  
Alkyl(perfluoroalkyl)phosphines

	Yield	Found (%)				Required (%)				Mol. wt.		Vapour pressure, $\log p$ (mm.) $= A - B/T$		Heat of vaporisation (cal./mole)	Trouton's constant	B.p. ( $\pm 1^\circ$ )
		C	H	F	P	C	H	F	P	Found	Reqd.	A	B			
$\text{Bu}^n(\text{CF}_3)_2\text{P}$ ...	78	31.8	4.2	50.3	13.6	31.9	4.0	50.4	13.7	225	226	7.89	1920	8790	22.9	110°
$\text{Bu}^i(\text{CF}_3)_2\text{P}$ ...	67	31.7	4.6	49.8	13.6	31.9	4.0	50.4	13.7	225	226	7.73	1800	8240	22.2	98
$\text{Bu}^n(\text{C}_3\text{F}_7)_2\text{P}$ ...	71	29.7	2.6		7.1	28.2	2.1		7.3	433 *	426	7.83	2210	10,110	22.7	173
$\text{Ph}(\text{C}_3\text{F}_7)_2\text{P}$ ...	47	32.7	1.7		6.9	32.3	1.1		7.0			7.96	2425	11,100	23.3	204
$\text{Bu}^n(\text{CF}_3)_2\text{P}$ ...	40	50.3	8.2	26.6	14.3	50.5	8.4	26.6	14.5	212 *	214	8.10	2300	10,530	23.9	167
$\text{Bu}^n(\text{CF}_3)\text{PCl}$	32	30.9	5.0	28.9	15.9	31.2	4.7	29.6	16.1	191	193	7.59	1894	8670	21.6	129
$\text{Et}_2(\text{C}_3\text{F}_7)_2\text{P}$ ...	34	32.6	4.1	51.2	11.2	32.6	3.9	51.6	12.0	253	258	7.98	2034	9310	23.3	126
$\text{Ph}_2(\text{C}_3\text{F}_7)_2\text{P}$ ...	20	50.8	3.0	37.3	8.8	50.8	2.8	37.6	8.8	346 *	354					
$(\text{CF}_3)_2(\text{C}_3\text{F}_7)_2\text{P}$	53	17.6	0.0	73.2	8.5	17.8	0.0	73.1	9.2	336	338	7.33	1543	7060	20.3	74

\* Cryoscopic.

Vapour pressure measurements (mercury isoteniscope) were reproducible, and none of the new compounds appeared to disproportionate. Molecular weights of volatile materials were obtained in the vacuum system. Analytical data are in Table I.

*Preparation of Phosphines.*—(a) *Methylbis(trifluoromethyl)phosphine.*  $(\text{CF}_3)_2\text{PCl}$  (2.01 g., 9.8 mmoles) was condensed on to a suspension of methyl-lithium (10.6 mmoles) in dimethyl ether at  $-78^\circ$ , and the mixture stirred for 2 hr.  $\text{Me}(\text{CF}_3)_2\text{P}$  (0.44 g., 24%) was isolated by fractional condensation [Found:  $\text{CF}_3$  (as  $\text{CF}_3\text{H}$ ), 74.1; P, 15.1%;  $M$ , 188. Calc. for  $\text{C}_3\text{H}_5\text{F}_6\text{P}$ :  $\text{CF}_3$ , 75.0; P, 16.8%;  $M$ , 184]. The infrared spectrum was identical with that described elsewhere.<sup>12</sup> In another experiment, using dibutyl ether as solvent,  $\text{Me}(\text{CF}_3)_2\text{P}$  was obtained (24%), together with butene and unidentified side-products. Diethyl ether is an unsuitable solvent since it is difficult to separate from the product.

(b) *n-Butylbis(trifluoromethyl)phosphine.*  $(\text{CF}_3)_2\text{PCl}$  (3.0 g., 14.7 mmoles) was condensed into a 50-ml. flask containing *n*-butyl-lithium (14.9 mmoles), hexane (10 ml.), and diethyl ether (10 ml.). A white solid precipitated as the mixture was stirred magnetically for  $\frac{1}{2}$  hr. at  $-78^\circ$ , and warmed slowly to room temperature. The volatile

the phosphine (0.852 mmole) and 1 equiv. of aqueous potassium hydroxide, only 0.237 mmole of trifluoromethane had formed during 1 week at  $20^\circ$ ; in a tube also containing ethanol (0.5 ml.), 0.686 mmole of trifluoromethane formed in 48 hr., showing that the reaction is considerably faster in a homogeneous medium.

(c) *Isobutylbis(trifluoromethyl)phosphine.*  $\text{Bu}^i(\text{CF}_3)_2\text{P}$  was prepared similarly from  $(\text{CF}_3)_2\text{PCl}$  and  $\text{BuLi}$ . Its reactions with water and an excess of aqueous alkali were like those of the *n*-butyl isomer.

(d) *Phenylbis(trifluoromethyl)phosphine.*<sup>6</sup> Phenyl-lithium (15 mmoles) and  $(\text{CF}_3)_2\text{PCl}$  (2.16 g., 10.6 mmoles), under the same conditions as used for the preparation of  $\text{Bu}(\text{CF}_3)_2\text{P}$ , gave  $\text{Ph}(\text{CF}_3)_2\text{P}$ , b.p.  $146$ – $148^\circ$  (1.41 g., 54%) [Found:  $\text{CF}_3$  (as  $\text{CF}_3\text{H}$ ), 55.1; P, 12.2. Calc. for  $\text{C}_8\text{H}_5\text{F}_6\text{P}$ :  $\text{CF}_3$ , 56.1; P, 12.6%]. In an experiment using only ether as solvent, the reaction was vigorous even at  $-78^\circ$ ; a tar (containing phosphorus and chlorine) was formed, and a reduced yield (27%) was obtained.

(e) *Butylbis(heptafluoropropyl)phosphine.*  $\text{Bu}(\text{C}_3\text{F}_7)_2\text{P}$  was obtained from  $(\text{C}_3\text{F}_7)_2\text{PCl}$ <sup>13</sup> and  $\text{BuLi}$ , and distilled, b.p.  $98$ – $100^\circ/56$  mm. (71%). A sample heated to  $140^\circ$  for 14 hr. was recovered quantitatively. The phosphine

<sup>8</sup> L. Maier, *Progr. Inorg. Chem.*, 1963, **5**, 27.

<sup>9</sup> D. Bryce Smith and E. E. Turner, *J. Chem. Soc.*, 1953, 861.

<sup>10</sup> J. A. Beel, H. C. Clark, and D. Whyman, *J. Chem. Soc.*, 1962, 4423.

<sup>11</sup> F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1953, 1565.

<sup>12</sup> M. A. A. Beg and H. C. Clark, *Canad. J. Chem.*, 1962, **40**, 393.

<sup>13</sup> H. J. Emeléus and J. D. Smith, *J. Chem. Soc.*, 1959, 375.

did not react with water at room temperature but traces of heptafluoropropane were detected after 48 hr. at 104°. Reaction with aqueous alkali was also slow. Thus, after 48 hr. at 116°, only 74% of the  $C_3F_7$  groups had been cleaved from phosphorus.

(f) *Phenylbis(heptafluoropropyl)phosphine*, b.p. 101°/36 mm., was made similarly from  $(C_3F_7)_3PCl$  and PhLi. It was recovered quantitatively after heating to 190°, and did not react with water at 130° or alkali at 20°. During 56 hr. at 130°, aqueous alkali cleaved 57% of the  $C_3F_7$  groups as  $C_3F_7H$ .

(g) *Dibutyl(trifluoromethyl)phosphine* and *butyl(trifluoromethyl)phosphinous chloride*. A mixture of  $CF_3PCl_2$  (2.0 g., 11.7 mmoles), BuLi (23.6 mmoles), hexane (10 ml.), and ether (5 ml.), after 2 hr. at -78°, yielded some yellow tar and a fine white precipitate of lithium chloride. Solvent was removed by rough fractional condensation, and the less volatile fractions, separated by distillation, were  $Bu(CF_3)PCl$ , b.p. 52°/62 mm. (0.23 g., 10%) and  $Bu_2(CF_3)P$ , b.p. 106—108°/62 mm. (1.01 g., 40%). In a similar experiment, 1 equiv. of BuLi in ether-hexane was added slowly during 2 hr. to  $CF_3PCl_2$ , and gave  $Bu(CF_3)PCl$  (32%) and  $Bu_2(CF_3)P$  (12%). The latter compound was first obtained (6%) by Cullen;<sup>3</sup> our sample was shown by analysis, b.p., and infrared spectrum to be identical with one prepared by his method.  $Bu(CF_3)PCl$  is a colourless liquid which fumes in air but does not spontaneously ignite. It gave trifluoromethane quantitatively (Found: 97.5%) with an excess of 20% sodium hydroxide solution after 24 hr. at room temperature. The phosphine  $Bu_2(CF_3)P$  did not react with water, even in a sealed tube at 134° (48 hr.), and was unattacked by 20% aqueous alkali at 25°. After 48 hr. with 20% sodium hydroxide solution at 124°, 18% hydrolysis was measured by  $CF_3H$  evolution.

(h) *Diethyl(heptafluoropropyl)phosphine*. A mixture of  $Et_2PCl$ <sup>14</sup> (3.0 g., 24.1 mmoles),  $C_3F_7I$  (7.4 g., 25.0 mmoles), and lithium (0.5 g., 72 mmoles) dispersed in ether (10 ml.) was stirred for 5 hr. at -60°. The volatile materials were separated by distillation, giving the product (2.1 g.), b.p. 124—125°, and uncharacterised higher-boiling material. The phosphine was readily oxidised by air but not spontaneously inflammable. A sample heated at 110° for 5 hr. in a sealed tube was recovered unchanged. The phosphine was also recovered quantitatively both after heating for 48 hr. with water in a sealed tube, and after shaking with aqueous 20% alkali for 5 days at 25°. After 48 hr. with 20% aqueous alkali at 130°, 31%, and after 56 hr. with potassium hydroxide in aqueous ethanol at 70°, 81% of the phosphine had been hydrolysed to heptafluoropropane.

(i) *Diphenyl(heptafluoropropyl)phosphine*.  $C_3F_7I$  (8.0 g., 27.0 mmoles) was condensed on to a mixture of  $Ph_2PCl$  (5.0 g., 22.7 mmoles), lithium dispersion (61.6 mmoles), and ether (10 ml.), and stirred at -60° for 16 hr. After removal of solvent and excess of  $C_3F_7I$ , the oily residue was extracted with ether, filtered, washed with water, and dried ( $Na_2SO_4$ ). The ether was removed and the phosphine distilled, b.p. 40°/10 mm.<sup>-3</sup>. A sample was apparently unchanged after 48 hr. at 50°, but was charred after 56 hr. at 190°. The phosphine was attacked only slowly by water or aqueous alkali at room temperature.

(j) *Heptafluoropropylbistrifluoromethylphosphine*. A mixture of  $(CF_3)_2PCl$  (2.6 g., 12.7 mmoles),  $C_3F_7I$  (3.64 g., 12.3 mmoles), ether (15 ml.), and lithium-2% sodium (28.6 mmoles) was stirred at -46° for 6 hr., and the product

separated in the vacuum system.  $(CF_3)_2(C_3F_7)P$  (2.26 g.) condensed at -46°, and was finally purified by high-vacuum distillation in a low-temperature column (reflux temperature -55°). The large excess of lithium used here was important since it destroyed most of the unreacted heptafluoroiodopropane which was difficult to separate from the phosphine.  $(CF_3)_2(C_3F_7)P$  is unaffected by mercury but spontaneously inflames in air. In its high volatility and low Trouton's constant, the phosphine is similar to tris(trifluoromethyl)-phosphine.<sup>12</sup>

The phosphine did not react with water below 80°, but a sample (0.558 mmole), with aqueous 20% potassium hydroxide, yielded a 2 : 1 mixture of trifluoromethane and heptafluoropropane (1.66 mmoles, 99% reaction) (Found:  $M$ , 101. Calc. for  $2CF_3H, C_3F_7H$ :  $M$ , 103). Another sample (0.624 mmole) was shaken in a sealed tube with sodium hydroxide (0.619 mmole) at 20°, and gave trifluoromethane (1.14 mmoles) contaminated with a trace of heptafluoropropane. The white solid obtained when the aqueous solution was freeze-dried for 2 days was sodium heptafluoropropylphosphonite<sup>13</sup> [Found: P, 10.7;  $C_3F_7$  (as  $C_3F_7H$ ), 58.7. Calc. for  $C_3F_7PH(O)ONa, 2H_2O$ : P, 10.6;  $C_3F_7$ , 57.9%].

(k) *Bisheptafluoropropyltrifluoromethylphosphine*.  $CF_3PCl_2$  (1.40 g., 8.19 mmoles),  $C_3F_7I$  (16.4 mmoles), and lithium-2% sodium (36 mmoles), in ether (11 ml.), were stirred for 4 hr. at -46°, and solvent was removed, leaving a slightly volatile liquid which was identified by its infrared spectrum as a mixture of mono- and di-substituted heptafluoropropyl derivatives. The liquid was distilled into dibutylamine to convert  $CF_3(C_3F_7)PCl$  into the involatile  $(CF_3)(C_3F_7)PNBu_2$  and *bisheptafluoropropyltrifluoromethylphosphine*, b.p. (estimated) 108—112° (15% yield based on  $CF_3PCl_2$ ), was pumped off (Found: C, 18.2; F, 69.1%;  $M$ , 410.  $C_7F_{17}P$  requires C, 19.2; F, 73.7%;  $M$ , 438). An attempt to recover  $(C_3F_7)(CF_3)PCl$  by treatment of the dibutylamino-derivative with an excess of hydrogen chloride (2 atm. at 25°) was not successful.

Bisheptafluoropropyltrifluoromethylphosphine is a colourless liquid, spontaneously inflammable in air. With an excess of alkali, a sample (0.335 mmole) gave a 1 : 2 mixture of trifluoromethane and heptafluoropropane (0.322 mmole) (Found:  $M$ , 131. Calc. for  $CF_3, 2C_3F_7H$ :  $M$ , 137).

*Heptafluoropropylbis(trifluoromethyl)phosphine Oxide*.—When gaseous  $(CF_3)_2(C_3F_7)P$  (1.40 mmoles) and nitrogen dioxide (1.40 mmoles) were mixed slowly, the colour faded during 3 hr. and the products were nitric oxide (1.40 mmoles) (Found:  $M$ , 29.6. Calc. for NO:  $M$ , 30) and *heptafluoropropylbis(trifluoromethyl)phosphine oxide*, b.p. 83—84°, v.p. 21 mm./0°, (97%), purified by column distillation in a vacuum with reflux at -47° (Found: C, 16.8; F, 69.2; P, 8.5%;  $M$ , 355.  $C_5F_{13}PO$  requires C, 16.9; F, 69.8; P, 8.8%;  $M$ , 354). The reaction is apparently quantitative only in the gas phase. When the reactants were sealed in a Pyrex ampoule and warmed to room temperature, an explosion resulted. When the reactants were mixed at low temperatures in the liquid phase, all the nitrogen dioxide was consumed, but the products, other than nitric oxide, were unchanged phosphine and unidentified brown material.

The phosphine oxide (0.294 g., 0.820 mmole) dissolved completely in water (3 ml.) at room temperature during 16 hr., and gave a mixture of  $CF_3H$  and  $C_4F_7H$  (0.799 mmole) (Found:  $M$ , 136, 34%  $CF_3H$ ), identified spectroscopically.

<sup>14</sup> K. Issleib and W. Seidel, *Chem. Ber.*, 1959, **92**, 2681.

TABLE 2

Infrared absorption frequencies (cm.<sup>-1</sup>)

Bu <sup>n</sup> (CF <sub>3</sub> ) <sub>2</sub> P (vapour):	2977s, 2947m, 2918sh,m, 2890m, 2250vw, 1467m, 1388m, 1270m,b, 1219s, 1198s, 1170vs, 1164sh,vs, 1142sh,vs, 1110vs, 1062m, 1029m, 1017sh,m, 974m, 887w, 855w, 815w, 786w, 728w
Bu <sup>i</sup> (CF <sub>3</sub> ) <sub>2</sub> P (vapour):	2980s, 2950m, 2890m, 1472m, 1392m, 1380w, 1245w, 1220sh,m, 1197vs, 1170sh,vs, 1161vs, 1144sh,vs, 1108vs, 1061w, 1027m, 950w, 840w, 799w, 726w
Bu <sup>n</sup> (C <sub>3</sub> F <sub>7</sub> ) <sub>2</sub> P (liquid film):	2965w, 2933w, 2875w, 1462w, 1382w, 1336m, 1270sh,m, 1231vs, 1211vs, 1180sh,s, 1136m, 1116s, 1104m, 1046w, 1019w, 894w, 836m, 746m, 738s, 666m
Ph(C <sub>3</sub> F <sub>7</sub> ) <sub>2</sub> P (liquid film):	3070w, 2320w, 1955w, 1482w, 1438m, 1355m, 1340sh,s, 1336s, 1265sh,m, 1228vs, 1209vs, 1181s, 1132s, 1113s, 1048m, 1028w, 1000w, 935sh,w, 910w, 838m, 749m, 738s, 692m, 670m, 665sh,w
Bu <sup>n</sup> (CF <sub>3</sub> )PCl (vapour):	2970m, 2940m, 2885m, 1468w, 1306w, 1177vs, 1155vs, 1126vs
Ph <sub>2</sub> (C <sub>3</sub> F <sub>7</sub> )P (liquid film):	3085w, 3065w, 1585w, 1475w, 1435m, 1330m, 1260m, 1229vs, 1208vs, 1180s, 1162m, 1138m, 1110s, 1073m, 1043w, 1029w, 1000w, 913w, 842m, 747s, 738s, 693s, 668m
(CF <sub>3</sub> ) <sub>2</sub> (C <sub>3</sub> F <sub>7</sub> )P (vapour):	1380w, 1342m, 1277m, 1244s, 1223sh,s, 1205vs, 1190vs, 1164vs, 1148sh,vs, 1138vs, 1116vs, 1055w, 845m, 745m, 675w, 560w, 530vw, 442m
(CF <sub>3</sub> ) <sub>2</sub> (C <sub>3</sub> F <sub>7</sub> )PO (vapour):	1360s, 1312s, 1282sh, 1248vs, 1232s, 1212vs, 1192vs, 1164sh, 1150w, 1127sh, 1120w, 1067w, 1022w, 990vw, 932w, 872m, 844w, 817w, 794vw, 744s, 712w, 677w, 655vw, 627vw, 602w, 562s, 530vw, 495sh, 480s, 442vw

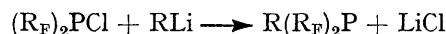
The resulting solution was treated with an excess of potassium hydroxide solution and gave a further quantity (0.819 mmole) of CF<sub>3</sub>H and C<sub>3</sub>F<sub>7</sub>H (Found: *M*, 98, 72% CF<sub>3</sub>H).

Bu<sup>n</sup>(CF<sub>3</sub>)<sub>2</sub>P, 55.9 (71.6); Bu<sup>i</sup>(CF<sub>3</sub>)<sub>2</sub>P, 55.4 (72.4); Ph(CF<sub>3</sub>)<sub>2</sub>P, 53.8 (80.2). Spectra of heptafluoropropylphosphines are described in Table 3.

**Hydrolysis Experiments.**—The hydrolyses of several perfluoroalkyl phosphorus compounds at 25.2° were followed by measuring the rates of evolution of trifluoromethane or heptafluoropropane using the apparatus described by Eaborn,<sup>15</sup> modified for use with readily oxidised materials. Samples were sealed in weighed fragile bulbs, which were broken under thermostatted solutions of alkali in aqueous ethanol (20% water by volume), and the volume (*V<sub>t</sub>*) of gas evolved at time *t* was recorded at intervals. The volume (*V<sub>F</sub>*) for complete reaction was calculated from the weight of phosphine taken. Concentrations of alkali and phosphine (*a*) were made equal, and second-order rate constants (*k<sub>2</sub>*), given by *k<sub>2</sub>* = *V<sub>t</sub>*/at(*V<sub>F</sub>* - *V<sub>t</sub>*), were obtained graphically from plots of *V<sub>t</sub>*/(*V<sub>F</sub>* - *V<sub>t</sub>*) against *t*. These plots were linear to 70% reaction. Results are in Table 4.

## DISCUSSION

Bis(perfluoroalkyl)phosphinous chlorides, (CF<sub>3</sub>)<sub>2</sub>PCl and (C<sub>3</sub>F<sub>7</sub>)<sub>2</sub>PCl, can be converted in 50–80% yield into the corresponding unsymmetrical tertiary phosphines R(R<sub>F</sub>)<sub>2</sub>P, by treatment with the organolithium reagents



at -78°. The reaction is inconveniently slow in pure hydrocarbons but proceeds readily in ether–hydrocarbon mixtures with more than 10% of ether. Best yields were obtained in 1 : 1 ether–hexane; the reaction was difficult

TABLE 3

<sup>19</sup>F Chemical shifts and coupling constants for heptafluoropropylphosphines

Compound	Chemical shifts (p.p.m.) <sup>a</sup>			Coupling constants (c./sec.)					
	α-CF <sub>3</sub>	β-CF <sub>2</sub>	γ-CF <sub>3</sub>	<sup>2</sup> J <sub>FFα</sub>	<sup>3</sup> J <sub>FFβ</sub>	<sup>4</sup> J <sub>FFγ</sub>	<sup>4</sup> J <sub>αγ</sub>	<sup>3</sup> J <sub>αβ</sub>	<sup>3</sup> J <sub>α3</sub>
Et <sub>2</sub> (CF <sub>3</sub> ) <sub>2</sub> CF <sub>2</sub> βCF <sub>2</sub> <sup>a</sup> P .....	116.2	124.7	81.2	45.7	24.8	8.7	10.1	3.3	V. small <sup>b</sup>
Ph <sub>2</sub> (C <sub>3</sub> F <sub>7</sub> )P .....	110.0	122.6	80.4	57.2	29.9	9.5	10.2	2.8	ca. 0.5
Bu(C <sub>3</sub> F <sub>7</sub> ) <sub>2</sub> P .....	110.0	123.4	80.7	46.7	31.1	7.9	10.5 <sup>c</sup>	— <sup>b</sup>	— <sup>b</sup>
(CF <sub>3</sub> ) <sub>2</sub> (CF <sub>3</sub> )CF <sub>2</sub> βCF <sub>2</sub> <sup>a</sup> P <sup>d</sup> .....	108.4	122.4	80.1	41.7	33.9	7.5	9.8	1.0	ca. 0.4
(CF <sub>3</sub> ) <sub>2</sub> (C <sub>3</sub> F <sub>7</sub> )PO <sup>e</sup> .....	116.8	122.5	80.3	86.0	2.2	2.8	9.8	1.2	V. small <sup>b</sup>

<sup>a</sup> Upfield from CFC1<sub>3</sub>. <sup>b</sup> Not observed. <sup>c</sup> From γ-CF<sub>3</sub> absorption only. <sup>d</sup> CF<sub>3</sub>-P, 48.2 p.p.m.; <sup>2</sup>J<sub>FFα</sub>, 86; <sup>4</sup>J<sub>αγ</sub>, 8.8; <sup>5</sup>J<sub>αβ</sub>, 4.8 c./sec. <sup>e</sup> CF<sub>3</sub>-P, 64.6 p.p.m.; <sup>2</sup>J<sub>FFα</sub>, 112; <sup>4</sup>J<sub>αγ</sub>, 7.4; <sup>5</sup>J<sub>αβ</sub>, 4.8 c./sec.

**Spectra.**—Infrared spectra (Table 2) were recorded on a Perkin-Elmer 337 spectrometer. <sup>19</sup>F N.m.r. spectra were obtained at 56.4 Mc./sec. on a Perkin-Elmer R10, or at

TABLE 4

Second-order rate constants (*k<sub>2</sub>*) for reaction between perfluoroalkyl phosphorus derivatives and alkali at 20.2°

Compound	Solvent	10 <sup>2</sup> Concn. (M)	<i>k<sub>2</sub></i> (M <sup>-1</sup> min. <sup>-1</sup> )
Bu <sup>n</sup> (CF <sub>3</sub> ) <sub>2</sub> P .....	<i>a</i>	4.12	0.75
Bu <sup>i</sup> (CF <sub>3</sub> ) <sub>2</sub> P .....	<i>a</i>	4.13	0.59
Ph(CF <sub>3</sub> ) <sub>2</sub> P .....	<i>a</i>	4.12	0.35 <sup>b</sup>
CF <sub>3</sub> PH(O)O <sup>-</sup> ...	Water	2.94	7.64
C <sub>3</sub> F <sub>7</sub> PH(O)O <sup>-</sup> ...	Water	2.89	9.95

<sup>a</sup> Water–20% ethanol 80%. <sup>b</sup> Rate plots slightly curved.

94.1 Mc./sec. on a Varian HA 100 instrument. Chemical shifts, in p.p.m. upfield from CFC1<sub>3</sub>, for trifluoromethyl phosphines are as follows. <sup>31</sup>P–<sup>19</sup>F coupling constants, *J* (c./sec.), are in parentheses. Bu<sup>n</sup><sub>2</sub>(CF<sub>3</sub>)P, 59.6 (58.8);

to control in pure ether. The function of the ether is presumably to complex the lithium alkyl or chloride; the gas-phase infrared spectrum of a mixture of bistrifluoromethylphosphinous chloride and ether showed no evidence of interaction. The ether and hydrocarbon solvents were chosen to aid separation of products, but tars formed easily in dibutyl ether and tetrahydrofuran. The phosphine Me(CF<sub>3</sub>)<sub>2</sub>P (b.p. 47°) was made in dimethyl ether at -78°, but only ca. 30% yields were obtained; in this case addition of hydrocarbon was unnecessary since the reaction is moderated by the low solubility of methyl-lithium.

The phosphines R(R<sub>F</sub>)<sub>2</sub>P and R<sub>2</sub>R<sub>F</sub>P would be accessible without recourse to high-pressure methods if perfluoroalkyl groups could be attached to phosphorus through lithium intermediates. We sought to explore this possibility by preparing heptafluoropropyl com-

<sup>15</sup> C. Eaborn, *J. Chem. Soc.*, 1955, 2517.



pounds, since trifluoromethyl Grignard or lithium reagents are not available. We used a procedure similar to that of Clark *et al.*<sup>10</sup> but found that commercial lithium was almost as satisfactory as lithium containing 2% of sodium. We confirmed that ether was the most satisfactory solvent, and that bistrifluoromethylphosphonous chloride did not react with lithium-sodium below  $-40^\circ$ . Phosphines with one  $\text{C}_3\text{F}_7$  group were made in yields of 20–50%, and those with two  $\text{C}_3\text{F}_7$  groups in lower yields (*ca.* 10%). These yields are comparable with those obtained by others<sup>16,17</sup> for comparable reactions.

The infrared absorptions at 1164 and 1105  $\text{cm}^{-1}$  in  $\text{Bu}_2(\text{CF}_3)\text{P}$ , and at 1177, 1155, and 1126  $\text{cm}^{-1}$  in  $\text{BuCF}_3\text{PCl}$ , may be assigned to the asymmetric and symmetric vibrations of the  $\text{CF}_3$  group. The phosphines  $(\text{CF}_3)_2\text{RP}$  ( $\text{R} = \text{Bu}, \text{Bu}^i$ ), like the Me and Ph compounds,<sup>11</sup> show four strong bands between 1225 and 1080  $\text{cm}^{-1}$ , associated with the  $(\text{CF}_3)_2\text{P}$  system. The spectra of heptafluoropropyl phosphorus compounds show 8–10 strong peaks between 1340 and 1020  $\text{cm}^{-1}$ ; the positions of these peaks (Table 5) do not vary very much as X is changed, but the higher-frequency peaks (1200–1340  $\text{cm}^{-1}$ ) are more intense and the peaks in the region 1020–1200  $\text{cm}^{-1}$  are broader in the compounds  $(\text{C}_3\text{F}_7)_2\text{PX}$  than in  $(\text{C}_3\text{F}_7)\text{PX}_2$ . There are also remarkably consistent strong absorptions at 740–750 and 665–672  $\text{cm}^{-1}$  in all  $\text{C}_3\text{F}_7\text{-P}$  compounds. The spectra of  $(\text{CF}_3)_2(\text{C}_3\text{F}_7)\text{P}$  and  $(\text{CF}_3)_2(\text{C}_3\text{F}_7)\text{PO}$  are almost identical except that peaks at 1312 and 480  $\text{cm}^{-1}$  in the spectrum of the phosphine oxide are absent from the spectrum of the phosphine. If these peaks can be associated with  $\text{>P=O}$  stretching and bending,<sup>18</sup> the electronegativity of the  $\text{C}_3\text{F}_7$  group, from Burg's relation,<sup>19</sup> is 2.8–2.5, assuming that the electronegativity of  $\text{CF}_3$ <sup>20</sup> is 3.3–3.5.

The  $^{19}\text{F}$  n.m.r. spectra of trifluoromethylphosphines consisted of doublets, from coupling between fluorine and phosphorus. The  $^{31}\text{P}$ – $^{19}\text{F}$  coupling constants in compounds  $\text{R}(\text{CF}_3)_2\text{P}$  decrease with increasing chemical shift, whereas in the halides  $(\text{CF}_3)_2\text{PX}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ), coupling constants increase with increasing shift.<sup>21</sup> Heptafluoropropylphosphines gave spectra with three well resolved bands, corresponding to  $\alpha$ -,  $\beta$ -, and  $\gamma$ -fluorine atoms, with the resonance due to  $\beta$ -fluorines at highest field. The  $^{31}\text{P}$ – $^{19}\text{F}$  coupling constants decrease as the number of intervening bonds increases, which may suggest that the dominant interaction between the nuclei is through the  $\text{P-C-C}\cdots$  chain. As in other fluorocarbon derivatives,<sup>22</sup>  $^{19}\text{F}$ – $^{19}\text{F}$  coupling constants

are largest between  $\alpha$ - and  $\gamma$ -fluorine atoms (*ca.* 10 c./sec.) and coupling constants between  $\alpha$ - and  $\beta$ - (*ca.* 3 c./sec.) and  $\beta$ - and  $\gamma$ - ( $<0.5$  c./sec.) fluorines are smaller. The absorption corresponding to the  $\alpha$ -fluorine atoms in the phosphine  $\text{Bu}(\text{C}_3\text{F}_7)_2\text{P}$  is a broad doublet with no fine-structure from coupling to the  $\gamma$ -fluorine atoms. There is no indication that the fluorines are inequivalent, as has been postulated for  $(\text{C}_3\text{F}_7)_2\text{PI}$ .<sup>23</sup>

The spectra of the phosphine  $(\text{CF}_3)_2(\text{CF}_3\gamma\text{CF}_2\beta\text{CF}_2\alpha)\text{P}$  and the phosphine oxide  $(\text{CF}_3)_2(\text{CF}_3\text{CF}_2\text{CF}_2)\text{PO}$  show four absorptions with intensities 6:3:2:2. Each is a complex multiplet, but the spectra can be completely interpreted on the assumptions that they are first-order. The  $^{19}\text{F}$ – $^{19}\text{F}$  coupling constants are larger for four intervening bonds (*e.g.*,  $^4J_{\alpha\alpha}$  or  $^4J_{\alpha\gamma}$ ) than for three (*e.g.*,  $^3J_{\alpha\beta}$  or  $^3J_{\beta\gamma}$ ) or five (*e.g.*,  $^5J_{\alpha\beta}$ ) or six (*e.g.*,  $^6J_{\alpha\gamma}$ ) bonds. In  $\text{CF}_3\gamma\text{CF}_2\beta\text{CF}_2\alpha\text{PF}_3$  the coupling constants<sup>23</sup> are:  $^3J_{\alpha\alpha}$  not observed;  $^4J_{\alpha\beta}$ , 7.9;  $^4J_{\alpha\gamma}$ , 9.3;  $^5J_{\alpha\gamma}$ , 1.5 c./sec. It does not seem to matter whether the intervening atoms are carbon or phosphorus; the maximum coupling between fluorines is observed when there are four intervening bonds, possibly when the interacting atoms can be closest. A similar large coupling constant ( $^4J_{\alpha\alpha}$ ) has been reported in the compound  $(\text{CF}_3)_2\text{NCF}_2\alpha\text{CF}_3$ .<sup>24</sup>

When the phosphine  $(\text{CF}_3)_2(\text{C}_3\text{F}_7)\text{P}$  is oxidised to the phosphine oxide, the resonances due to  $\text{F}_\beta$  and  $\text{F}_\alpha$  move to higher field and the phosphorus-fluorine coupling constants ( $^2J_{\text{PF}}$  and  $^2J_{\text{PF}\alpha}$ ) increase. Similar changes have been noted<sup>21</sup> when the phosphine  $(\text{CF}_3)_3\text{P}$  is oxidised, and seem to occur generally when the co-ordination number of the phosphorus is increased.<sup>25,26</sup> The coupling constants  $^3J_{\text{PF}\beta}$  and  $^4J_{\text{PF}\gamma}$  are markedly less in the phosphine oxide than in the phosphine.

TABLE 5

Infrared frequencies ( $\text{cm}^{-1}$ ) of heptafluoropropyl phosphorus compounds

$(\text{C}_3\text{F}_7)_2\text{PX}$ ( $\text{X} = \text{Bu}, \text{Ph}; ^a \text{I}, \text{Cl}, \text{NH}_2, \text{OEt}; ^b \text{F}^c$ )
$(\text{C}_3\text{F}_7)\text{PX}_2$ ( $\text{X} = \text{Et}, \text{Ph}; ^a \text{I}, \text{Cl}; ^b \text{F}; ^c \text{SiMe}_3$ )
1336–1350; 1255–1280; 1225–1240; 1210–1225;
1180–1192; 1130–1160; 1105–1125; <sup>e</sup> 1040–1065;
1020–1030; 740–750; 665–672

<sup>a</sup> This work. <sup>b</sup> H. J. Emeléus and J. D. Smith, unpublished. <sup>c</sup> Ref. 23. <sup>d</sup> Ref. 26. <sup>e</sup> Usually two peaks in  $(\text{C}_3\text{F}_7)_2\text{PX}$ .

Most of the information available on the hydrolysis of perfluoroalkyl phosphorus compounds<sup>2,6,12,13,27</sup> has been derived from sealed-tube reactions. It has not been possible to decide how much the slower cleavage of heptafluoropropyl compared with trifluoromethyl<sup>13,16</sup> results from the lower solubility of the heptafluoropropyl derivatives in water. In the present work an attempt has been made to compare rates of hydrolysis under

<sup>23</sup> J. F. Nixon, *J. Chem. Soc.*, 1965, 777.

<sup>24</sup> A. Saika and H. S. Gutowsky, *J. Amer. Chem. Soc.*, 1956, 78, 4818.

<sup>25</sup> J. F. Nixon, *J. Chem. Soc. (A)*, 1967, 1136; C. G. Barlow and J. F. Nixon, *Inorg. Nuclear Chem. Letters*, 1966, 2, 323, and unpublished observations.

<sup>26</sup> D. J. Holman and J. D. Smith, unpublished.

<sup>27</sup> F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1954, 3896.

<sup>16</sup> H. C. Clark, J. T. Kwon, and D. Whyman, *Canad. J. Chem.*, 1963, 41, 2628.

<sup>17</sup> R. D. Chambers, W. K. R. Musgrave, and J. Savory, *J. Chem. Soc.*, 1962, 1993.

<sup>18</sup> A. B. Burg and A. J. Sarkis, *J. Amer. Chem. Soc.*, 1965, 87, 238.

<sup>19</sup> J. E. Griffiths and A. B. Burg, *J. Amer. Chem. Soc.*, 1962, 84, 3442.

<sup>20</sup> J. J. Lagowski, *Quart. Rev.*, 1959, 13, 233.

<sup>21</sup> K. J. Packer, *J. Chem. Soc.*, 1963, 960.

<sup>22</sup> J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' vol. 2, Pergamon, London, 1966.

homogeneous conditions, in aqueous ethanol. The phosphines  $R(CF_3)_2P$  are hydrolysed by 20% aqueous alkali with almost quantitative liberation of both trifluoromethyl groups as trifluoromethane. The compounds  $R(C_3F_7)_2P$  and  $R_2(CF_3)P$  are hydrolysed much less easily, but, even under homogenous conditions, the rate of formation of heptafluoropropane is slower than that of trifluoromethane by several powers of ten. With 1 equivalent of alkali in aqueous ethanol, the phosphines  $R(CF_3)_2P$  yielded 1 equivalent of trifluoromethane, and gave good second-order rate plots to 70% reaction, with the rate constants decreasing in the order  $R = Bu^n > Bu^i > Ph$ , but discussion of these must await the measurement of activation parameters, since the differences in the rates of hydrolysis of other phosphorus compounds have been shown to reflect differences in both activation energy and entropy.<sup>28</sup> The phosphine  $Ph(C_3F_7)_2P$  appears to be less readily hydrolysed than  $Bu(C_3F_7)_2P$ , but rate measurements have not been obtained.

The isolation of the unsymmetrical trisperfluoroalkylphosphine  $(CF_3)_2(C_3F_7)P$  has made possible experiments

on the relative ease of cleavage of trifluoromethyl and heptafluoropropyl groups. Thus, with 1 equivalent of alkali, both trifluoromethyl groups were liberated as trifluoromethane, and sodium heptafluoropropylphosphonite was obtained almost quantitatively. The phosphine oxide  $(CF_3)_2(C_3F_7)PO$ , with water, gave both trifluoromethane and heptafluoropropane, suggesting that in this compound the rates of cleavage of trifluoromethyl and heptafluoropropyl are comparable. Similarly, from measurements on perfluoroalkylphosphonites, which have the phosphinate structure  $R_FHP(O)O^-$ , the second-order rate constants for the formation of trifluoromethane and heptafluoropropane under similar conditions (Table 4) were almost the same. These results may reflect differences in mechanism for hydrolysis of ter- and quinque-valent phosphorus compounds.

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<sup>28</sup> J. R. Cox and D. B. Ramsay, *Chem. Rev.*, 1964, **64**, 317.