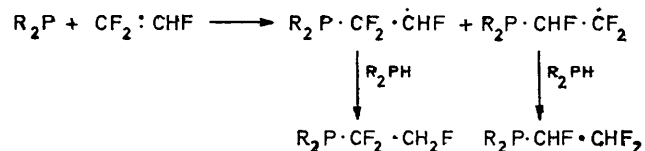# Organophosphorus Chemistry. Part XVII.[1] Reaction of Hexafluoropropene and Some Fluorochloro-olefins with Phosphines: Competition between Radical and Ionic Reactions

By Peter Cooper, Roy Fields, and Robert N. Haszeldine,* Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Dimethylphosphine reacts nucleophilically with hexafluoropropene to give *trans-* and *cis-*dimethylpentafluoropropenylphosphines in proportions which depend on the reaction conditions. These products do not arise by dehydrofluorination of a 1 : 1 adduct. The same dimethylpentafluoropropenylphosphines are also produced in good yield by the reaction of tetramethyldiphosphine with hexafluoropropene. Bistrifluoromethylphosphine failed to react with hexafluoropropene. Dimethylphosphine gives the 1 : 1 adduct 2,2-dichloro-1,1-difluoroethyldimethylphosphine and 2,2-dichloro-1-fluorovinyldimethylphosphine *via* nucleophilic attack on 1,1-dichloro-difluoroethylene to give $Me_2\overset{+}{P}H \cdot CF_2 \cdot \overset{-}{C}Cl_2$ followed by proton transfer and loss of fluoride ion respectively. Phosphine and bistrifluoromethylphosphine give 1 : 1 adducts with 1,1-dichlorodifluoroethylene by radical reactions in which the phosphinyl radicals attack predominantly or exclusively the CF_2 group. 1-Chloro-2-fluoroethylene reacts rather inefficiently with dimethylphosphine, both nucleophilic and radical attack giving 2-chloro-1-fluoroethyldimethylphosphine. Radical attack by bistrifluoromethylphosphine gives 2-chloro-1-fluoroethylbistrifluoromethylphosphine, together with several other products.

THE free-radical reactions of phosphines R_2PH with trifluoroethylene give two-way addition,[2] the proportion of attack on the CF_2 group increasing along the series $R = CF_3 < H < CH_3$; in free-radical reactions with vinyl fluoride and 1,1-difluoroethylene, dimethylphosphine gives two-way addition,[3] although phosphine[4] and bistrifluoromethylphosphine [3] give only single products. These results have been interpreted [2b,3] in terms of the susceptibility of the sites in the olefins to nucleophilic

attack and changes in the electrophilic character of the attacking radicals with change in the substituent group R.

$$R_2P \cdot + CF_2 \! : \! CHF \longrightarrow R_2P \cdot CF_2 \cdot \dot{C}HF + R_2P \cdot CHF \cdot \dot{C}F_2$$

$$\downarrow R_2PH \qquad\qquad \downarrow R_2PH$$

$$R_2P \cdot CF_2 \cdot CH_2F \qquad R_2P \cdot CHF \cdot CHF_2$$

Hexafluoropropene is known [4] to undergo two-way addition on photochemical reaction with phosphine, and

[1] Part XVI, R. Brandon, R. N. Haszeldine, and P. J. Robinson, *J.C.S. Perkin II*, 1973, 1301.

[2] (a) R. Fields, H. Goldwhite, R. N. Haszeldine, and J. Kirman, *J. Chem. Soc. (C)*, 1966, 2075; (b) R. Fields, R. N. Haszeldine, and N. F. Wood, *ibid.*, 1970, 744.
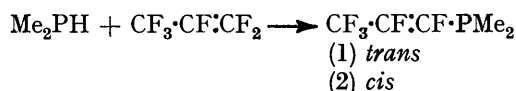
[3] R. Fields, R. N. Haszeldine, and N. F. Wood, *J. Chem. Soc. (C)*, 1970, 1370.

[4] G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J. Chem. Soc.*, 1963, 1083.
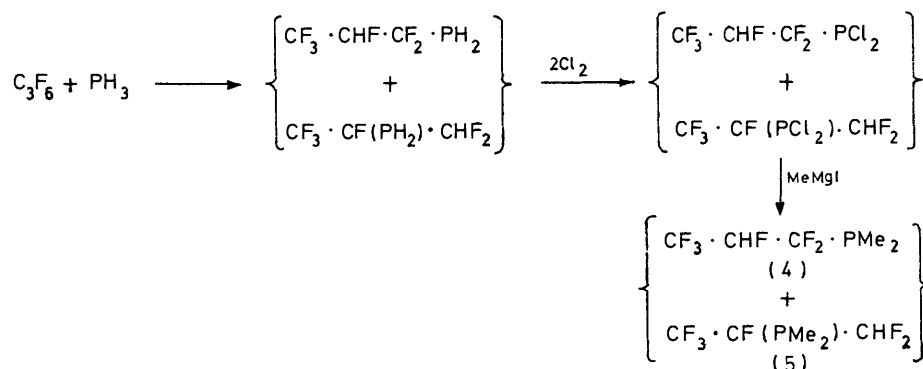
we now report a study of the reaction of hexafluoropropene with bistrifluoromethylphosphine and with dimethylphosphine, and of these phosphines with some fluorochloro-olefins.

Hexafluoropropene.—Nucleophilic attack on hexafluoropropene occurs exclusively at the CF_2 group, but radical attack by PH_2 is bidirectional. Since the bistrifluoromethylphosphinyl radical is more electrophilic than the phosphinyl radical, a lower proportion of attack by the fluoroalkylphosphinyl radical on the CF_2 group of hexafluoropropene might be expected; conversely, the less electrophilic dimethylphosphinyl radical should give a higher proportion of attack on the CF_2 group than does [4] the phosphinyl radical (66%). In the event, the reaction between bistrifluoromethylphosphine and hexafluoropropene failed under normal irradiation conditions, and even after prolonged irradiation the only detectable reactions were hydrogenation of the double bond and formation of tetrakistrifluoromethyldiphosphine and of trifluoromethane. The reaction of phosphine with hexafluoropropene is slow, and presumably reaction at the $CF_3 \cdot CF$ group of the olefin is inhibited by the size of the bistrifluoromethylphosphinyl radical, and that at the CF_2 group by the enhanced electrophilicity of the radical.

In contrast, dimethylphosphine reacted readily when irradiated with hexafluoropropene, but the product was not the expected mixture of 1 : 1 adducts, and was shown by i.r. and n.m.r. spectroscopy and by mass spectrometry to be a 70 : 30 mixture of *trans*- and *cis*-dimethylpentafluoropropenylphosphines (1) and (2), respectively. The same compounds were formed at a similar rate, but
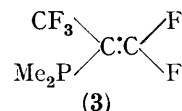
$$Me_2PH + CF_3 \cdot CF \colon CF_2 \longrightarrow CF_3 \cdot CF \colon CF \cdot PMe_2$$

(1) *trans*
(2) *cis*

in rather different proportions (95 : 5) at 50° (estimated to be the temperature within a reaction tube during an

was clearly shown by the 144 Hz F–F coupling constant to be the *trans*-isomer (1), a pure sample of which was obtained from a reaction of hexafluoropropene with tetramethyldiphosphine (see below). The minor product was assigned the *cis*-structure (2), rather than that with geminal fluorine atoms (3) since the isomer ratio could

(3)

readily be changed either by irradiation of the isomer mixture, or at 250°. Further evidence for the *cis*-structure (2) was obtained from the ^{19}F n.m.r. spectrum, which showed no CF_3–F coupling of the size required for fluorine *cis* to a trifluoromethyl group [21·0 Hz in (1)]. The F–F coupling (4—5 Hz) could be identified only by spin-decoupling experiments; the magnitude is reasonable in view of the low ' group contribution ' reported [5] for the trifluoromethyl group and that derived for the PX_2 group from couplings reported [6] for olefins containing such substituents.

In order to test whether the olefinic phosphines (1) and (2) were formed by dehydrofluorination under the influence of dimethylphosphine of an initially formed 1 : 1 adduct (4), a mixture of the 1 : 1 adducts (4) and (5) was prepared, albeit in low yield, by chlorination and methylation of the mixture of 1 : 1 adducts obtained by the photochemical reaction of phosphine with hexafluoropropene; the reaction conditions were analogous to those previously described [4] for the preparation of 2-chloro-1,1,2-trifluoroethyldimethylphosphine from 2-chloro-1,1,2-trifluoroethylphosphine. Although some decomposition of the adducts (4) and (5) took place when they were kept at 55° with dimethylphosphine, it was clear that no dehydrofluorination to (1) and (2) took place. The formation of these products in the reaction of hexafluoropropene with dimethylphosphine is thus
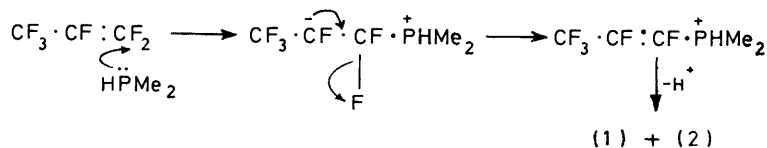

irradiation) in the dark, indicating that the reaction involves nucleophilic attack on the olefin by dimethylphosphine, since free radical reactions of the phosphine do not proceed measurably at this temperature.

G.l.c. separation of the products was not possible, and the product ratio was estimated from repeated integrations of the ^{19}F n.m.r. signals. The major product.

most satisfactorily explained by nucleophilic attack by dimethylphosphine on the CF_2 group of the olefin, followed by expulsion of fluoride ion from the carbanion so formed (Scheme 1), although the precise relationship
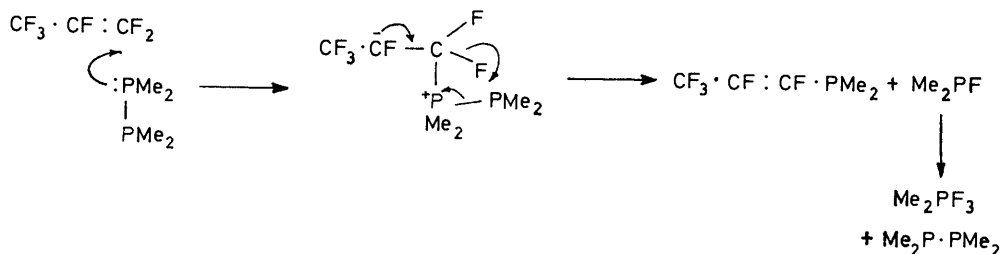
[5] M. G. Barlow, *Chem. Comm.*, 1966, 703.
[6] A. H. Cowley and M. W. Taylor, *J. Amer. Chem. Soc.*, 1969, **91**, 1026.

between the reaction conditions and the ratio of (1) : (2) is not clear.

The photochemical addition of phosphine to hexafluoropropene required a very long reaction time, and gave an isomer ratio of 62% $CF_3 \cdot CHF \cdot CF_2 \cdot PH_2$ to 38% $CF_3 \cdot CF(PH_2) \cdot CHF_2$, in good agreement with the 66 : 34 ratio reported,[4] but quite different from that reported [7] for the thermal (150°) reaction, the product of which was

identified by its n.m.r. spectrum [10] as the phosphinic fluoride, presumably formed from the phosphorane during work-up by traces of moisture, together with an unidentified compound which the ¹H spectrum showed to contain the Me_nP^V group.

Chlorofluoroethylenes.—Dimethylphosphine reacted readily in the dark at 60° with 1,1-dichlorodifluoroethylene, to give a mixture of compounds which were partially

SCHEME 1

SCHEME 2

identified from its ¹H n.m.r. spectrum as mainly $CF_3 \cdot CF(PH_2) \cdot CHF_2$, although no parameters were given.* In view of the rapid reaction of dimethylphosphine at the CF_2 group of hexafluoropropene by a non-radical route, the dark reaction of phosphine with hexafluoropropene was also checked, but after 25 days at 50° both starting materials were recovered quantitatively. The possibility that the isomer ratio observed for the photochemical addition has been distorted by a non-radical addition reaction is thus excluded. N.m.r. parameters for the hexafluoropropyl-phosphines, -phosphonous dichlorides, and -dimethylphosphines are reported in the Experimental section.

Tetramethyldiphosphine reacts readily under u.v. irradiation with a range of olefins[1,8] to give 1,2-bisdimethylphosphinoethane derivatives, but when hexafluoropropene was irradiated with tetramethyldiphosphine a 94 : 6 mixture of (1) and (2) was obtained in 94% yield. A reaction in the dark at 50° gave the pure *trans*-isomer (1) in 97% yield. Since tetramethyldiphosphine fails to react in the dark at 50° with other olefins,[8] the reaction with hexafluoropropene must again involve nucleophilic attack on the CF_2 group of the olefin, followed presumably by intramolecular transfer of fluorine from carbon to phosphorus to give dimethylphosphinous fluoride (Scheme 2); under the reaction conditions the latter gives [9] the phosphorane observed in the photochemical reaction. The product from the thermal reaction was

separated by g.l.c. and identified by their n.m.r. and mass spectra as 2,2-dichloro-1-fluorovinyldimethylphosphine (37%) and 2,2-dichloro-1,1-difluoroethyldimethylphosphine (45%), together with involatile material. Thus nucleophilic attack on this olefin may be followed either by loss of fluoride ion or, in contrast to the reactions with hexafluoro- or with 1,1,3,3,3-pentafluoro-propene,[3] by transfer of a proton (Scheme 3).
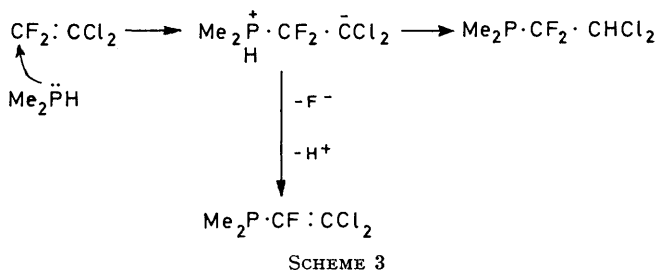
SCHEME 3

There was no detectable reaction between 1,1-dichlorodifluoroethylene and either phosphine or bistrifluoromethylphosphine in the dark at 50°. On irradiation, phosphine gave a good yield of 2,2-dichloro-1,1-difluoroethylphosphine (84%), together with some 2% of an impurity identified in the mixture by the characteristic ¹⁹F n.m.r. doublet of its CHF_2 group, further split into doublets by the β-phosphorus, as 1,1-dichloro-2,2-di-

* In our hands (experiment by Mr. K. Morris) a dark reaction in a sealed tube at 150° gave a 3 : 2 ratio (by ¹⁹F n.m.r. integration) of $CF_3 \cdot CHF \cdot CF_2 \cdot PH_2$: $CF_3 \cdot CF(PH_2) \cdot CHF_2$ but the major product (*ca.* three times the yield of the phosphines) was 1*H*,2*H*-perfluoropropane.

[7] G. W. Parshall, D. C. England, and R. V. Lindsey, *J. Amer. Chem. Soc.*, 1959, **81**, 4801.

[8] P. Cooper, R. Fields, and R. N. Haszeldine, *J. Chem. Soc.* (C), 1971, 3031.

[9] F. Seel, K. Rudolph, and W. Gombler, *Angew. Chem. Internat. Edn.*, 1967, **6**, 708.

[10] R. Schmutzler, *J. Chem. Soc.*, 1964, 4551.

fluoroethylphosphine. The phosphines were converted

$$PH_3 + CF_2{:}CCl_2 \longrightarrow CHCl_2{\cdot}CF_2{\cdot}PH_2 + CHF_2{\cdot}CCl_2{\cdot}PH_2$$

into the corresponding phosphonous dichlorides in good yield (only the major isomer being detectable by n.m.r.), but the reaction with methylmagnesium iodide gave a very low yield of the dimethylphosphino-compounds, thus frustrating an attempt to investigate their stability towards dehydrofluorination.

Under u.v. irradiation bistrifluoromethylphosphine gave only a low yield (32%) of 2,2-dichloro-1,1-difluoro-ethylbistrifluoromethylphosphine, together with products of breakdown of bistrifluoromethylphosphine (tristri-fluoromethylphosphine, trifluoromethane, and tetrakis-trifluoromethyldiphosphine) and a low yield of a complex mixture of volatile products and involatile material which was shown not to include 1,2-di(bistrifluoromethyl-phosphino)-1,1-dichlorodifluoroethane. The latter was prepared in a separate experiment [8] from the olefin and tetrakistrifluoromethyldiphosphine. Radical attack on

$$(CF_3)_2P{\cdot}P(CF_3)_2 + CF_2{:}CCl_2 \overset{u.v.}{\longrightarrow}$$
$$(CF_3)_2P{\cdot}CF_2{\cdot}CCl_2{\cdot}P(CF_3)_2$$
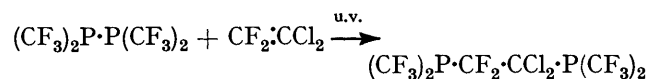
1,1-dichlorodifluoroethylene is thus overwhelmingly at the CF_2 group, even with the highly electrophilic bistrifluoro-methylphosphinyl radical, indicating the overriding importance of intermediate radical stabilisation in these reactions.

The photochemical reaction between dimethylphos-phine and 1-chloro-2-fluoroethylene gave a low yield of a single 1 : 1 adduct, 2-chloro-1-fluoroethyldimethylphos-phine. The same compound was formed in the dark at 50°, but in a slower reaction, judged by the olefin re-covered (64% vs. 30%), and in substantially lower yield (4%, cf. 24% in the photochemical reaction). Thus most of the product in the photochemical reaction must be due to radical attack on the CHF group, although the form-ation of a small part of the product by a non-radical 'dark' reaction, with nucleophilic attack at the CHF group, seems likely. 1-Chloro-2-fluoroethylene fre-quently produces high-boiling material in reactions with free radical sources (e.g. with phosphine [2a]), or when ir-radiated alone,[11] and similar reactions may account for much of the high-boiling material produced in these reac-tions. In addition, a separate experiment showed that high-boiling material was readily produced when the 1 : 1 adduct was heated.

The photochemical reaction of bistrifluoromethylphos-phine with 1-chloro-2-fluoroethylene led to an even more complex mixture of products, only two of which, apart from known products from the irradiation of the phos-phine alone, could be identified by their n.m.r. spectra after g.l.c. separation, as the expected 1 : 1 adduct, 2-chloro-1-fluoroethylbistrifluoromethylphosphine, and 2-

chloro-2-fluoroethylbistrifluoromethylphosphine, the formation of which must involve an unusual migration of chlorine. The considerable number of unidentified com-pounds in the reaction mixture prevents conclusions about the relative importance of attack at the CHF or the CHCl group.

It is clear from the reactions of the three olefins re-ported here that it is possible for nucleophilic attack by dimethylphosphine to compete effectively with attack by the dimethylphosphinyl radical when the substrate olefin is reasonably susceptible to nucleophilic attack (C_3F_6, $CF_2{:}CCl_2$, $CF_3{\cdot}CH{:}CF_2$,[3] and, to a much smaller extent, CHF:CHCl). It has been shown not to occur with vinyl fluoride,[3] 1,1-difluoroethylene,[3] or trifluoro-ethylene,[2a] under the normal conditions for radical attack. The last result is important since any nucleophilic attack would invalidate the conclusions concerning the propor-tion of radical attack at either end of the double bond. The slow dark-reaction of tetrafluoroethylene [12] with di-methylphosphine at 100° may also be due to nucleophilic attack. Neither phosphine nor bistrifluoromethylphos-phine has shown any indication of nucleophilic reaction with any of the olefins so far studied.

EXPERIMENTAL

Phosphine,[13] dimethylphosphine,[14] bistrifluoromethyl-phosphine,[15] and tetramethyldiphosphine [16] were prepared by published methods. All operations with the phosphorus compounds were carried out in vacuo or under a blanket of dry nitrogen. All irradiations were carried out in silica tubes with Hanovia UVS 500 medium pressure mercury arc lamps. I.r. spectra were obtained using a Perkin-Elmer 257 grating spectrometer, mass spectra with an A.E.I. MS2 or MS902 mass spectrometer, and n.m.r. spectra with a Perkin-Elmer R10 spectrometer at 60·00 (^{1}H), 56·46 (^{19}F) and 24·29 (^{31}P) MHz. Chemical shifts are given in p.p.m. to low field (positive) of external references, benzene (neat liquid) for ^{1}H, trifluoroacetic acid for ^{19}F, and phosphoric acid for ^{31}P, except where stated. Integrated intensities were in all cases in accord with the assignments given. Analyses were carried out by the microanalytical laboratory of this depart-ment, work in which has shown [17] that organophosphorus compounds of the type described here require higher tem-peratures and longer time for complete combustion than is normally required. With these precautions, satisfactory analyses were obtained. Molecular weights were measured by Regnault's method (M) or mass spectrometrically (M^+).

Reactions of Hexafluoropropene with Dimethylphosphine.—
(a) *Photochemical.* Dimethylphosphine (1·85 g, 29·8 mmol) and hexafluoropropene (4·47 g, 29·8 mmol) were irradiated (120 h, 50°) to give traces of hydrogen and silicon tetra-fluoride, recovered hexafluoropropene (1·56 g, 35%), a mixture (Found: C, 31·3; H, 3·3%; M^+, 192. Calc. for $C_5H_6F_5P$: C, 31·2; H, 3·1%; M, 192) of trans-*dimethyl-pentafluoroprop-1-enylphosphine* (1) (2·14 g, 57% on olefin consumed), δ_F +9·0 (3F, ddd, CF_3), −76·0 (1F, dqd, PCF:), and −86·4 (1F, ddq, $CF_3{\cdot}CF{:}$), δ_H −2·4 (dt, Me_2P),

[11] R. Fields, R. N. Haszeldine, and J. Kirman, unpublished results.
[12] R. Fields, R. N. Haszeldine, and J. Kirman, *J. Chem. Soc.* (C), 1970, 197.
[13] A. R. Stiles, F. F. Rust, and W. E. Vaughan, *J. Amer. Chem. Soc.*, 1952, **74**, 3282.
[14] G. W. Parshall, personal communication, 1963; *Inorg. Synth.*, 1968, **11**, 157.
[15] F. W. Bennett, H. J. Eméleus, and R. N. Haszeldine, *J. Chem. Soc.*, 1953, 1565; R. G. Cavell and R. C. Dobbie, *J. Chem. Soc.* (A), 1967, 1308.
[16] H. Niebergall and B. Langenfeld, *Chem. Ber.*, 1962, **95**, 64.
[17] G. J. Kakabadse and B. Manohin, unpublished results.

$J_{\text{F-F-}trans}$ 144·4, $J_{\text{CF}_3\text{-F-}gem}$ 10·0, $J_{\text{CF}_3\text{-F-}cis}$ 21·0, $J_{\text{CF}_3\text{-P}}$ 2·8, $J_{\text{P-F-}gem}$ 2·3, $J_{\text{P-F-}cis}$ 58·9, and $J_{\text{P-OH}_2}$ 4·8 Hz, and the cis-isomer (2) (0·96 g, 26% on olefin consumed), δ_F +12·2 (3F, ddd, CF$_3$), −60·6 (1F, complex, :CF), and −62·0 (1F, complex, :CF), $J_{\text{CF}_3\text{-P}}$ 58·8, $J_{\text{CF}_3\text{-F-}trans}$ 11·3, and $J_{\text{CF}_3\text{-F-}gem}$ 7·6 Hz; solid material (1·6 g) containing fluoride ion remained in the reaction tube.

(b) *At 50°.* Dimethylphosphine (0·46 g, 7·4 mmol) and hexafluoropropene (1·12 g, 7·5 mmol), after 100 h in the dark (50°), gave hexafluoropropene (0·24 g, 21%), a mixture of (1) and (2) (1·09 g, 97% on olefin consumed) in the ratio 95 : 5, and a solid (ca. 0·2 g).

Attempted Reaction of Hexafluoropropene with Bistrifluoromethylphosphine.—(a) *Photochemical.* Bistrifluoromethylphosphine (2·30 g, 13·5 mmol) and hexafluoropropene (2·02 g, 13·5 mmol) gave, after irradiation (22 days) *in vacuo*, hydrogen (0·53 mmol), recovered olefin (1·73 g, 86%), recovered phosphine (1·60 g, 70%), trifluoromethane (0·17 g, 59% on phosphine consumed), hexafluoropropane (0·21 g, 71% on olefin consumed), and slightly impure tetrakistrifluoromethyldiphosphine (0·4 g).

(b) *Thermal.* The olefin (1·21 g, 8·1 mmol) and the phosphine (1·37 g, 8·1 mmol) were recovered quantitatively after being kept together *in vacuo* at 100° in the dark (120 h).

Reaction of Hexafluoropropene with Tetramethyldiphosphine.—(a) *Photochemical.* Irradiation (48 h) of hexafluoropropene (2·35 g, 15·7 mmol) and tetramethyldiphosphine (1·87 g, 15·4 mmol) gave a little dimethylphosphine, trifluorodimethylphosphorane (1·02 g, 56% on original diphosphine), identified by its ^{1}H and ^{19}F n.m.r. spectra,[18] and a mixture of *trans-* and *cis*-dimethylpentafluoroprop-1-enylphosphine (2·78 g, 94%) in the ratio 94 : 6.

(b) *Thermal.* Tetramethyldiphosphine (1·75 g, 14·3 mmol) and hexafluoropropene (2·24 g, 15·0 mmol) gave, after 120 h in the dark (50°), dimethylphosphinic fluoride, identified by its ^{1}H and ^{19}F n.m.r. spectra,[10] and an unidentified compound [δ_H −5·1 (d, *J* 17 Hz)], and *trans*-dimethylpentafluoroprop-1-enylphosphine (2·79 g, 97%) (Found: *M*, 194), b.p. (isoteniscope) 92·8°, L_v 7·91 kcal mol^{-1}, Trouton's constant 21·6 cal K^{-1} mol^{-1}, *m/e* 192 (M^+), 127 ($C_3H_3F_3P$), 69 (CF_3), and 65 (CH_3FP), $\nu_{\text{C:C}}$ 1684m cm^{-1}.

Dark Reaction of Phosphine and Hexafluoropropene.—Phosphine (0·36 g, 10·6 mmol) and hexafluoropropene (1·58 g, 10·5 mmol) were recovered unchanged after 600 h at 50° in the dark.

Preparation of the Hexafluoropropyldimethylphosphines (4) *and* (5).—The photochemical reaction of hexafluoropropene with phosphine (cf. ref. 4) gave a mixture (0·93 g; isomer ratio 62 : 38) of 1,1,2,3,3,3-hexafluoropropylphosphine, δ_F +2·2 (complex, CF$_3$), −14·6 (AB pattern, J_{AB} 306 Hz, CF$_2$), and −128·2 (d, $J_{\text{F-H-}gem}$ 43·7 Hz, CFH), δ_H −2·2 (CFH), −3·4 (d, $^1J_{\text{PH}}$ 203; t, $^3J_{\text{H-CF}_2}$ 19·5; d, $^4J_{\text{H-CF}}$ 5·2; q, $^5J_{\text{H-CF}_3}$ 1·2 Hz; PH$_2$), δ_P −133 (t, *J* 205; t, $^2J_{\text{P-CF}_2}$ 79 Hz); and (1-difluoromethyltetrafluoroethyl)phosphine, δ_F +0·4 (CF$_3$), −51 (CF$_2$H), and −98·6 (d, $^2J_{\text{P-CF}}$ 91·4 Hz, CF), δ_H −0·9 (t, $J_{\text{F-H-}gem}$ 55·8; d, $^3J_{\text{H-CF}}$ 5·6; d, $^3J_{\text{HP}}$ 2·4 Hz, CF$_2$H), and −3·3 (d, $^1J_{\text{PH}}$ 204, d, $^3J_{\text{H-CF}}$ 24 Hz; PH$_2$), δ_P −154 (td). The mixture and chlorine (0·73 g, 10·3 mmol) were condensed at separate levels in a Pyrex tube (300 ml), and the tube was sealed *in vacuo* at −196° and allowed to warm from −95° overnight, to give, after removal of the excess of chlorine (Hg), hydrogen chloride (0·37 g, 100%), and a mix-

ture (0·97 g, 76%; isomer ratio 2 : 1) of 1,1,2,3,3,3-hexafluoropropylphosphonous dichloride, δ_F * +2·2 (CF$_3$), −43·6 (AB pattern, J_{AB} 290 Hz, CF$_2$), and −140·2 (CHF), δ_H * −1·7 (d, $J_{\text{F-H-}gem}$ 43·8 Hz, CHF); and (1-difluoromethyltetrafluoroethyl)phosphonous dichloride, δ_F * +7·4 (CF$_3$), −53·4 (CF$_2$H), and −102·2 (d, J_{FP} 89 Hz, CF), δ_H * −0·5 (t, $J_{\text{H-F-}gem}$ 52·8 Hz, CF$_2$H). This mixture (0·95 g, 3·75 mmol) was added to an ethereal solution of methylmagnesium iodide [from methyl iodide (3·0 g)], and heated under reflux (1 h) to give, after conventional work-up, a mixture (0·128 g, 16%; isomer ratio 3 : 1) (Found: M^+, 212. Calc. for $C_5H_7F_6P$: *M*, 212) of dimethyl-1,1,2,3,3,3-hexafluoropropylphosphine, δ_F −76·0 (d, *J* 14·4; d, *J* 11·3; d, *J* 11·3; d, *J* 9·3; d, *J* 6·2 Hz, CF$_3$), −120·2 (complex AB pattern, J_{AB} 294 Hz, $v_0\delta$ 6·2 p.p.m., CF$_2$), −200 (complex d, *J* 42 Hz, CFH) (shifts in p.p.m. from CFCl$_3$ solvent), δ_H −5·6 (d, J_{POH} 4·2 Hz, PCH$_3$); and 1-difluoromethyltetrafluoroethyldimethylphosphine, δ_F * −73·6 (CF$_3$), −129·8 (d, *J* ca. 50 Hz, CF$_2$H) (shifts in p.p.m. from CFCl$_3$ solvent; CFP group not resolved), δ_H −5·5 (overlapping with band from major isomer) and −0·9 (t, 55, d, 6, d, 4 Hz, CF$_2$H).

Reaction of the Hexafluoropropyldimethylphosphines with Dimethylphosphine.—The hexafluoropropylphosphines (4) and (5) (0·0216 g, 0·10 mmol) and dimethylphosphine (0·0094 g, 0·15 mmol) were recovered quantitatively after 115 h at room temperature in a sealed Pyrex tube (5 ml). After 210 h at 55°, the volatile material (0·19 mmol, 76%) was unchanged, but a small amount of involatile material was formed.

Reaction of Dimethylphosphine with 1,1-Dichlorodifluoroethylene.—Dimethylphosphine (1·36 g, 21·9 mmol) and 1,1-dichlorodifluoroethylene (2·94 g, 22·1 mmol) were kept in the dark at 60° (120 h) to give unchanged olefin (0·62 g, 21%), dimethylphosphine (0·13 g, 10%), involatile solid and liquid material, and a volatile mixture (2·66 g). G.l.c. separation of the mixture gave a pure component, identified spectroscopically as 2,2-dichloro-1-fluorovinyldimethylphosphine (1·12 g, 37%) (Found: M^+, 174 with isotope pattern corresponding to the presence of two chlorine atoms. Calc. for $C_4H_6Cl_2FP$; *M*, 174), δ_F −31·6 (d, $J_{\text{F-P-}gem}$ 34·7 Hz), δ_H −5·4 (d, $J_{\text{P-CH}_2}$ 4·9 Hz), and 2,2-dichloro-1,1-difluoroethyldimethylphosphine (1·54 g, 45%) (Found: M^+, 194 with isotope pattern corresponding to the presence of two chlorine atoms. Calc. for $C_4H_7Cl_2F_2P$; *M*, 194), δ_F −33·8 (d, $^2J_{\text{PF}}$ 40·0, d, $^3J_{\text{F-OH}}$ 8·9 Hz, CF$_2$P), δ_H −0·77 (t, *J* 9·0, d, $^3J_{\text{HP}}$ 1·2 Hz, CHCl$_2$) and −5·4 (d, $J_{\text{P-OH}_3}$ 4, t, $^4J_{\text{CH}_2\text{-CF}_2}$ 0·6 Hz, Me$_2$P), containing in addition a little of the first component.

Reaction of Bistrifluoromethylphosphine with 1,1-Dichlorodifluoroethylene.—(a) *Photochemical.* Bistrifluoromethylphosphine (4·0 g, 23·5 mmol) and the olefin (2·91 g, 21·9 mmol) were irradiated *in vacuo* (240 h) to give trifluoromethane (0·37 g), tristrifluoromethylphosphine (1·43 g), recovered olefin (0·38 g, 13%), a mixture (0·6 g) containing tetrakistrifluoromethyldiphosphine together with some seven other components, 2,2-dichloro-1,1-difluoroethylbistrifluoromethylphosphine (1·83 g, 32% on olefin consumed) (Found: C, 15·6; H, 0·6%; M^+, 302. $C_4HCl_2F_8P$ requires C, 15·8; H, 0·3%; *M*, 302), b.p. 115—118° at 731 mmHg, δ_F +27·8 [d, $J_{\text{P-CF}_3}$ 83·2, t, $^4J_{\text{CF}_3\text{-CF}_2}$ 8·5 Hz, (CF$_3$)$_2$P] and −21·2 (d, $J_{\text{CF}_2\text{-P}}$ 47·9 Hz, of octets $^3J_{\text{CF}_2\text{-H}}$ = $^4J_{\text{CF}_3\text{-CF}_2}$ = 8·5 Hz, CF$_2$P), δ_H −0·8 (t, $^3J_{\text{CF}_2\text{-H}}$ 8·8, d, $^3J_{\text{HP}}$ 2·0 Hz, CHCl$_2$), and an unidentified viscous liquid (1·03 g).

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* All the bands showed further complex, well-resolved splitting. Only the major coupling constants are given here.

[18] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, 1963, **2**, 613.

(b) *Thermal.* Bistrifluoromethylphosphine (2·06 g, 12·1 mmol) and 1,1-dichlorodifluoroethylene (1·61 g, 12·1 mmol) were recovered quantitatively after being kept *in vacuo* at 50° (120 h).

Reaction of Phosphine with 1,1-*Dichlorodifluoroethylene and the Preparation of* 2,2-*Dichloro*-1,1-*difluoroethylphosphonous Dichloride.*—(a) *Photochemical.* Phosphine (0·71 g, 21·0 mmol) and the olefin (2·79 g, 21·0 mmol) were irradiated (120 h) to give hydrogen (0·3 mmol), phosphine (0·29 g, 41%), unchanged olefin (1·18 g, 42%), and a mixture (1·73 g, 86% on olefin consumed) of 2,2-dichloro-1,1-difluoroethylphosphine (98%) and a compound tentatively identified from its ^{19}F spectrum [δ_F −45·6 (d, $^2J_{CF_2H}$ 56·4 Hz, of d, $^3J_{CF_2-P}$ 8·5 Hz)] as 1,1-dichloro-2,2-difluoroethylphosphine (2%) (Found: C, 14·7; H, 1·7%; *M*, 167. Calc. for $C_2H_3Cl_2F_2P$: C, 14·4; H, 1·8%; *M*, 167), b.p. (isoteniscope) 88° (lit.,[7] 109·5—110·5°), L_v 8·59 kcal mol^{-1}, Trouton's constant 23·8 cal K^{-1} mol^{-1}, δ_F −9 (d, $^2J_{P-CF_2}$ 70·5, t, $J_{H_2P-CF_2}$ 17·2, d, $^3J_{CF_2-H}$ 8·2 Hz, CF$_2$P), δ_H −2·95 (d, $^1J_{PH}$ 204, t, J, 17·2 Hz, PH$_2$) and −0·75 (t, J 8·1, d, $^4J_{PH}$ 2·0 Hz, CHCl$_2$).

The phosphines (2·95 g, 17·7 mmol) and chlorine (2·52 g, 35·4 mmol) were condensed *in vacuo* at two levels in a Pyrex tube, and the tube was sealed and allowed to warm slowly from −78°. After removal of the excess of chlorine, hydrogen chloride (1·18 g, 91%), 1,1-dichloro-2,2-difluoroethylene (0·20 g), unidentified volatile material (2·7 mmol) (Found: *M*, 147), 2,2-*dichloro*-1,1-*difluoroethylphosphonous dichloride* (3·14 g, 75%) (Found: C, 10·0; H, 0·5%; *M*$^+$, 234. $C_2HCl_4F_2P$ requires C, 10·3; H, 0·4%; *M*, 234), δ_F −35·4 (d, $^2J_{CF_2P}$ 69·8, d, $^3J_{CF_2-H}$ 9·0 Hz, CF$_2$P), δ_H −0·18 (t, J 9·1, d, $^3J_{HP}$ 1·0 Hz, CHCl$_2$), and a trace of material presumed to be the corresponding tetrachlorophosphorane ($^2J_{PF}$ 127 Hz) were isolated.

(b) *Thermal.* Phosphine (0·36 g, 10·5 mmol) and 1,1-dichlorodifluoroethylene (1·40 g, 10·5 mmol) were recovered (98% each) after 120 h at 50° in the dark. No other products could be detected.

Reaction of 1-*Chloro*-2-*fluoroethylene with Dimethylphosphine.*—(a) *Photochemical.* Dimethylphosphine (3·13 g, 50·5 mmol) and 1-chloro-2-fluoroethylene (3·47 g, 43·1 mmol) were irradiated (120 h) *in vacuo* to give traces of hydrogen and recovered dimethylphosphine, recovered olefin (1·19 g, 34%), 2-*chloro*-1-*fluoroethyldimethylphosphine* (0·97 g, 24%

on olefin consumed) (Found: C, 33·4; H, 6·6%; *M*$^+$, 142. C_4H_9ClFP requires C, 33·7; H, 6·3%; *M*, 142), δ_F (94·1 MHz) −124 (d, $^2J_{FH}$ 49·5, d, $^2J_{FP}$ 48, d, $^3J_{FH}$ 21, d, $^3J_{FH}$ 24 Hz), δ_H (100 MHz) +5·05 (d, J 49·5 Hz, CHF), +3·96 (complex pattern, CH$_2$Cl), both showing second order distortion, +1·37 and +1·32 [2 d, $^2J_{POH_2}$ 3·6 Hz, which coalesced to a triplet (3·6 Hz) at 60 MHz, PMe$_2$ group] (shifts in p.p.m. from Me$_4$Si lock signal), and unidentified solid material (4·5 g) (Found: C, 44·4; H, 9·1%) which was insoluble in common solvents and decomposed rapidly in the presence of acetone.

(b) *Thermal.* Dimethylphosphine (1·52 g, 24·5 mmol) and 1-chloro-2-fluoroethylene (1·99 g, 24·7 mmol), kept *in vacuo* at 50° (125 h), gave recovered olefin (1·28 g, 64%), dimethylphosphine (0·82 g, 54%), 2-chloro-1-fluoroethyl-dimethylphosphine (0·05 g, 4% on olefin consumed), and solid material.

Action of Heat on 2-*Chloro*-1-*fluoroethyldimethylphosphine.*—The phosphine (0·056 g, 0·70 mmol) was kept *in vacuo* at 100° (165 h) to give a glassy solid and no volatile material.

Reaction of 1-*Chloro*-2-*fluoroethylene with Bistrifluoromethylphosphine.*—(a) *Photochemical.* Bistrifluoromethylphosphine (5·92 g, 34·8 mmol) and the olefin (2·80 g, 34·8 mmol) were irradiated *in vacuo* (240 h) to give hydrogen (0·35 mmol), trifluoromethane (0·90 g), bistrifluoromethylphosphine (1·28 g, 22%), 1-chloro-2-fluoroethylene (0·54 g, 19%), a complex mixture (3·27 h) containing at least 14 components, from which two were isolated by preparative g.l.c. and tentatively identified from their n.m.r. spectra as 2-chloro-1-fluoroethylbistrifluoromethylphosphine, δ_F +26 [2 d, $^2J_{POF_2}$ 71·3 of q, J 5·6 Hz, $(CF_3)_2P$ groups in a dissymmetric environment] and −116br (complex, CHF), δ_H −1·1 (d, $^2J_{FH}$ 46, t, $^3J_{HH}$ 5 Hz, CHF), and −2·7 (d, $^3J_{FH}$ 24, t, $^3J_{HH}$ = $^3J_{PH}$ 5 Hz, CH$_2$Cl) and 2-chloro-2-fluoroethylbistrifluoromethylphosphine, δ_F +22·6 [d, $^2J_{POF_2}$ 76·1, d, J 2·8 Hz, $(CF_3)_2P$] and −49 (d, $^2J_{FH}$ 48, q, $^3J_{FH} \approx {}^3J_{FP}$ 17 Hz, CHFCl), δ_H −0·4 (d, J 50, q, $^3J_{HH} \approx {}^3J_{PH}$ 5 Hz, CHFCl group) and −3·8 (d, J 17, d, J 5·5, d, $^2J_{PH}$ 2 Hz, CH$_2$), and brown solid and viscous liquid material (*ca.* 1·4 g).

(b) *Thermal.* Bistrifluoromethylphosphine (1·33 g, 7·8 mmol) and the olefin (0·63 g, 7·8 mmol) were recovered quantitatively after 120 h in the dark at 100°.