Organophosphorus Chemistry. Part IX.[1] Reaction of Dimethyl- and Bis(trifluoromethyl)-phosphines with Olefins

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Dimethyl- and bis(trifluoromethyl)-phosphines react smoothly with olefins under u.v. irradiation to give products $R^1_2PR^2$ ($R^1 = CF_3$, R^2 = Et, Pr^n, Bu^n, CHMeEt, or $CF_2{\cdot}CHF_2$; R^1 = Me, R^2 = Et, $CF_2{\cdot}CHF_2$, or $CF_2{\cdot}CHFCl$) which are in accord with a free-radical mechanism in which the phosphino-radical $R^1_2\dot{P}$ attacks the olefin to give the most stable intermediate radical.

The tertiary phosphines containing the $(CF_3)_2P$ group readily liberate fluoroform almost quantitatively with aqueous base, but those containing the Me_2P group are more resistant to hydrolysis.

FREE-RADICAL addition of phosphine to fluoro-olefins has been described earlier;[2] the reaction has now been extended to additions of the secondary phosphines dimethylphosphine (to ethylene, tetrafluoroethylene, and chlorotrifluoroethylene) and bis(trifluoromethyl)-phosphine (to ethylene, propene, but-1-ene, *trans*-but-2-ene, and tetrafluoroethylene). The phosphines do not react with these olefins in the dark at 40°, but under u.v. illumination at this temperature smoothly give the corresponding tertiary phosphines in high yield, *e.g.*,

$$R_2\dot{P} \xrightarrow{\text{olefin}} R_2P[\text{olefin}\dot{]} \xrightarrow{R_2PH} R_2P[\text{olefin}]H + R_2\dot{P}$$

$R = CF_3$; olefin $= CH_2{:}CH_2,\ CH_2{:}CHMe,\ CH_2{:}CHEt,$ *trans*-$MeCH{:}CHMe,\ CF_2{:}CF_2$

$R = Me$; olefin $= CH_2{:}CH_2,\ CF_2{:}CF_2,\ CF_2{:}CFCl$

Since the product contains no P–H bond, its further reaction with olefin, as has been observed in the reaction of phosphine with tetrafluoroethylene,[2a] is not possible. With unsymmetrical olefins, such as propene, but-1-ene, or chlorotrifluoroethylene, the products were exclusively those formed by attack of the phosphino-radical to give the more stable intermediate radical, *e.g.* $(CF_3)_2P{\cdot}CH_2{\cdot}\dot{C}HMe$ rather than $(CF_3)_2P{\cdot}CHMe{\cdot}\dot{C}H_2$. Products which would have resulted from radical addition in the opposite sense were sought, and would have been detected in the reactions with propene and with chlorotrifluoroethylene in concentrations greater than about 1—2%, and in the but-1-ene reaction in concentrations greater than 4%.

The yield of ethylbis(trifluoromethyl)phosphine, based on ethylene consumed, was almost quantitative, and under the correct conditions, near-quantitative conversion of olefin was achieved. Traces of hydrogen, fluoroform (1%), and 1,1,1-trifluoropropane (1%) formed during the irradiation presumably arise as follows:

$$\begin{tikzcd}
EtP(CF_3)_2 \arrow[r] & Et\dot{P}{\cdot}CF_3 + \dot{C}F_3 \arrow[r, "RH"] \arrow[d, "C_2H_4"] & CHF_3 \\
& CF_3{\cdot}CH_2{\cdot}\dot{C}H_2 \arrow[r, "RH"] & CF_3{\cdot}CH_2{\cdot}CH_3
\end{tikzcd}$$

Over-irradiation led to a decrease in the yield of ethylbis(trifluoromethyl)phosphine, with corresponding increase in the yields of trifluoromethane, trifluoropropane, and high-boiling material. Bis(trifluoromethyl)-phosphine and ethylene did not react in the absence of light even at 100°, thus making an ionic mechanism for the photochemical reaction seem unlikely.

Hydrolysis of ethylbis(trifluoromethyl)phosphine with concentrated aqueous sodium hydroxide, known[3] to liberate fluoroform quantitatively from methylbis-(trifluoromethyl)phosphine, gave only a low (16%) yield of fluoroform at 80°, but addition of a small amount of dioxan increased the yield of fluoroform to two moles per mole of the tertiary phosphine, presumably by increasing miscibility of the reactants.

Bis(trifluoromethyl)phosphine reacted more rapidly with propene, as expected in view of the increased electron density at the double bond; the 1 : 1 adduct was formed in 99% yield, with complete consumption of the olefin, after only 1 hr. Again there was no reaction in the absence of light. Gas chromatographic examination of the product, with use of several columns and sets of operating conditions, gave no indication that more than one component was present. The ^1H n.m.r. spectrum of the product was complex, but showed no signals attributable to the isopropyl group, and the

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[1] Presented in part at the Third International Symposium on Fluorine Chemistry, Munich, 1965; Part VIII, M. Green, R. N. Haszeldine, and G. S. A. Hopkins, *J. Chem. Soc.* (*A*), 1966, 1766.

[2] (*a*) G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J. Chem. Soc.*, 1963, 1083; (*b*) R. Fields, H. Goldwhite, R. N. Haszeldine, and J. Kirman, *J. Chem. Soc.*, 1966, 2075.

[3] R. N. Haszeldine and B. O. West, *J. Chem. Soc.*, 1957, 3880.

i.r. spectrum showed no sign of an isopropyl doublet at 7·22 μm.

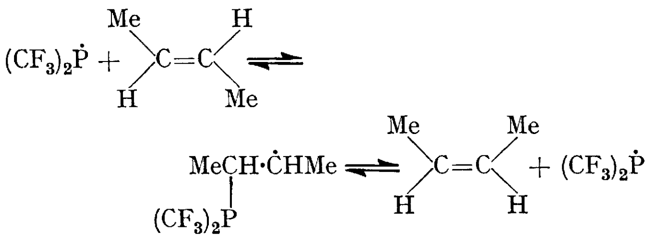
But-1-ene and *trans*-but-2-ene also reacted rapidly with bis(trifluoromethyl)phosphine under irradiation, and 89% of the olefin was consumed after 1 hr. in each case. The but-2-ene can give only 1-methylpropylbis-(trifluoromethyl) phosphine, which is also the product which would be obtained from but-1-ene if attack occurred at C-2.

$$\mathrm{MeCH{:}CHMe} \xrightarrow{(\mathrm{CF_3})_2\mathrm{PH}} (\mathrm{CF_3})_2\mathrm{P{\cdot}CHEtMe}$$

$$\mathrm{EtCH{:}CH_2} \xrightarrow{(\mathrm{CF_3})_2\mathrm{PH}} (\mathrm{CF_3})_2\mathrm{P{\cdot}Bu^n}\ \text{or}\ (\mathrm{CF_3})_2\mathrm{P{\cdot}CHEtMe}$$

Gas chromatography did not differentiate between the products from the two reactions, since the retention times differed by only a few seconds, and a synthetic mixture of the two products could not be resolved. The i.r. and ^{1}H n.m.r. spectra, however, were markedly different. In particular, a strong band at τ 8·83 in the ^{1}H n.m.r. spectrum of the product from but-2-ene was completely absent from that of the product from but-1-ene, indicating that attack had taken place at least 96—98% (since 2—4% of the 1-methylpropyl compound would have been detected) at the terminal carbon atom of but-1-ene.

The formation of *cis*-but-2-ene in the reaction of bis-(trifluoromethyl)phosphine with *trans*-but-2-ene indicates that the addition of this phosphino-radical is reversible like those of $\mathrm{Ph\dot{P}H}$, $\mathrm{Bu^n_2\dot{P}}$, and $\mathrm{NC{\cdot}CH_2{\cdot}CH_2{\cdot}\dot{P}H}$ radicals.[4]



In contrast to the reactions with hydrocarbon olefins, the reaction of bis(trifluoromethyl)phosphine with tetrafluoroethylene was slow, and 75% of the olefin and of the phosphine was recovered after irradiation for 1 hr. 1,1,2,2-Tetrafluoroethylbis(trifluoromethyl)phosphine was isolated in 98% yield (based on the phosphine consumed). Tetrafluoroethylene and bis(trifluoromethyl)phosphine did not react in the dark at 40°, but at 200° gave the tertiary phosphine (68% on phosphine consumed) together with considerable amounts of perfluorocyclobutane and fluoroform.

The alkylbis(trifluoromethyl)phosphines were readily hydrolysed by a mixture of 40% aqueous sodium hydroxide and dioxan at 80°, to give fluoroform essentially quantitatively. The tetrafluoroethylphosphine also liberated tetrafluoroethane:

$$\mathrm{CHF_2{\cdot}CF_2{\cdot}P(CF_3)_2} \xrightarrow{\text{aq. NaOH}} \mathrm{CHF_2{\cdot}CHF_2 + 2CHF_3}$$

All of the tertiary bis(trifluoromethyl)phosphines studied had a strong i.r. band at 8·27—8·40 μm. and a broad band, sometimes resolved into a doublet, between 8·60 and 8·74 μm., presumably caused by the $\mathrm{P(CF_3)_2}$ group. The ^{19}F n.m.r. absorption of trifluoromethyl groups was in the range 21—29 p.p.m. to low field of external trifluoroacetic acid, and was usually a doublet owing to coupling with the adjacent phosphorus atom ($J_{\mathrm{PCF_3}}$ 71—79 Hz). In the 1-methylpropylphosphine, the ^{19}F absorption was complex owing, presumably, to the asymmetric carbon adjacent to the phosphorus.

Dimethylphosphine, readily prepared in good yield by reduction of tetramethyldiphosphine disulphide with lithium aluminium hydride,[5] reacted photochemically with tetrafluoroethylene to give dimethyl-1,1,2,2-tetrafluoroethylphorphine. Dimethylphosphine and tetrafluoroethylene did not react at room temperature in the dark, but at 100° the dimethyltetrafluoroethylphosphine (92% on olefin consumed) was produced slowly.

$$\mathrm{Me_2PH + C_2F_4} \xrightarrow{\text{u.v.}} \mathrm{Me_2P{\cdot}CF_2{\cdot}CHF_2}\ (69\%) + \mathrm{CHF_2{\cdot}CHF_2}\ (4\%)$$

Dimethylphosphine reacted readily when irradiated with ethylene, to give ethyldimethylphosphine, and with chlorotrifluoroethylene to give 2-chloro-1,1,2-trifluoroethyldimethylphosphine, both in good yield. The latter was identical with a sample prepared by the following route:[2a]

$$\begin{tikzcd}
\mathrm{CF_2{:}CFCl + PH_3} \arrow[r, "\text{u.v.}"] & {} \\
\mathrm{H_2P{\cdot}CF_2{\cdot}CHFCl} \arrow[r, "2\mathrm{Cl_2}"] & \mathrm{Cl_2P{\cdot}CF_2{\cdot}CHFCl} \arrow[d, "2\mathrm{MeMgI}"] \\
& \mathrm{Me_2P{\cdot}CF_2{\cdot}CHFCl}
\end{tikzcd}$$

The addition of phosphine to chlorotrifluoroethylene was shown[2a] by halogenation and pyrolysis to give only 2-chloro-1,1,2-trifluoroethylphosphine, and the n.m.r. spectra of the chlorotrifluoroethyldimethylphosphine prepared by the two methods showed no trace of 1-chloro-1,2,2-trifluoroethyldimethylphosphine which would have been formed had the addition taken place in the opposite sense.

The dimethylpolyfluoroethylphosphines were resistant to hydrolysis by aqueous sodium hydroxide even in the presence of dioxan at 90°. After 6 hr., 2-chloro-1,1,2-trifluoroethyldimethylphosphine gave 1-chloro-1,2,2-trifluoroethane (6%), trifluoroethylene (14%) and unchanged phosphine; under these conditions, as in the hydrolysis[6] of the phosphonous dichloride $\mathrm{CHFCl{\cdot}CF_2{\cdot}PCl_2}$, the olefin could arise by dehydrochlorination of the alkane.

$$\mathrm{CHFCl{\cdot}CHF_2} \xrightarrow{\mathrm{OH^-}} \mathrm{CHF{:}CF_2}$$

Dimethyltetrafluoroethylphosphine gave only a 5%

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[4] J. Pellon, *J. Amer. Chem. Soc.*, 1961, **83**, 1915.

[5] G. W. Parshall, personal communication, 1963; *Inorg. Synth.*, 1968, **11**, 157.

[6] G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J. Chem. Soc.*, 1964, 572.

yield of tetrafluoroethane, but treatment with ethanolic potassium hydroxide at 85° gave 1,1,2,2-tetrafluoroethane almost quantitatively.

EXPERIMENTAL

All transfers of phosphines were carried out *in vacuo*, with use of conventional vacuum apparatus, or under nitrogen. Irradiations were carried out in silica tubes (*ca.* 300 ml.) with Hanovia U.V.S. 500 lamps at temperatures of 35—40°. N.m.r. spectra were obtained with either an A.E.I. RS2 (60 MHz) or a Perkin-Elmer R10 spectrometer (60 MHz for ^{1}H, 56·46 MHz for ^{19}F). Chemical shifts for ^{19}F are in p.p.m. to high field (+ve) of external trifluoroacetic acid unless another reference is specified. The signs of the coupling constants have not been determined.

The olefins (except propene, which was made by dehydration of propan-2-ol) were commercial samples, which were distilled *in vacuo* before use, and shown to be at least 99% pure by g.l.c. and i.r. spectroscopy.

Bis(trifluoromethyl)phosphine.—Bis(trifluoromethyl)phosphine, prepared (65%) by Raney nickel catalysed reduction of bis(trifluoromethyl)phosphinous iodide,[7] had $\lambda_{\text{max.}}$ (vap.) 253—259 nm. (ε *ca.* 4), $\lambda_{\text{min.}}$ 237 nm. (ε *ca.* 2), and rising absorption below 237 nm. The n.m.r. spectrum showed absorption at τ 5·46 (J_{HP} 216, J_{HF} 9·7 Hz) for ^{1}H, at 47·6 p.p.m. to high field of trichlorofluoromethane (J_{PF} 69 Hz) for ^{19}F, and at 49·8 p.p.m. to high field of phosphoric acid for ^{31}P.

Reaction of Bis(trifluoromethyl)phosphine with Ethylene.—Bis(trifluoromethyl)phosphine (2·60 g., 15·3 mmoles) and ethylene (0·43 g., 15·3 mmoles) were irradiated (6 hr.) to give hydrogen (<0·1 mmole), a mixture of ethylene (0·004 g., 1%) and fluoroform (0·02 g., 1%), 1,1,1-trifluoropropane (0·03 g., 1%), *ethylbis(trifluoromethyl)phosphine* (2·92 g., 97%) (Found: C, 24·5; H, 2·7%; *M*, 198. $C_4H_5F_6P$ requires C, 24·2; H, 2·6%; *M*, 198), b.p. 62—63°/763 mm., and a small amount (0·04 g.) of unidentified higher-boiling material. The ^{1}H n.m.r. spectrum showed absorption at τ 8·73 (3H, overlapping d and t, Me) and 7·92 (2H, q). The ^{19}F spectrum showed a strong doublet at −21·3 p.p.m. (J_{FP} 71·2 Hz).

Similar irradiation for 1 hr. gave hydrogen (<0·1 mmole), ethylene (0·17 g., 39%), fluoroform (0·001 g., <1%), bis(trifluoromethyl)phosphine (0·99 g., 38%), 1,1,1-trifluoropropane (0·001 g., 1%), ethylbis(trifluoromethyl)phosphine (1·85 g., 98% on olefin consumed), and higher-boiling material (0·05 g.). Irradiation for 50 hr. gave hydrogen (0·3 mmole), fluoroform (0·08 g., 4%) with possibly a small amount of ethane (<1%), a mixture of bis(trifluoromethyl)phosphine (0·07 g., 3%) and 1,1,1-trifluoropropane (0·09 g., 6%), ethylbis(trifluoromethyl)phosphine (2·53 g., 84%), and higher-boiling material (0·19 g.).

Ethylene (0·43 g., 15·3 mmoles) and bis(trifluoromethyl)phosphine (2·60 g., 15·3 mmoles) were recovered quantitatively after being kept in the dark at 40° (50 hr.) and at 100° (6 hr.).

Reaction of Bis(trifluoromethyl)phosphine with Propene.—Bis(trifluoromethyl)phosphine (2·61 g., 15·4 mmoles) and propene (0·65 g., 15·4 mmoles) were irradiated (1 hr.) to give hydrogen (<0·1 mmole), propene (0·005 g., 1%) and a trace of fluoroform, bis(trifluoromethyl)phosphine (0·015 g., 1%), *n-propylbis(trifluoromethyl)phosphine* (3·20 g., 99% on olefin consumed) (Found: C, 28·6; H, 3·5%; *M*, 212. $C_5H_7F_6P$ requires C, 28·3; H, 3·3%; *M*, 212), b.p. 85°/748 mm., and higher-boiling material (0·01 g.). Gas chromatographic examination of the tertiary phosphine with use of a number of columns and temperatures showed only one peak. The ^{1}H n.m.r. spectrum was complex; the ^{19}F spectrum showed a doublet (J_{FP} 71·2 Hz) at −22·6 p.p.m.

Bis(trifluoromethyl)phosphine and propene were recovered quantitatively after being kept together in the dark at 40° (24 hr.).

Reaction of Bis(trifluoromethyl)phosphine with other Olefins.—Irradiation (1 hr.) of bis(trifluoromethyl)phosphine with equimolar amounts of the following olefins gave in each case a small amount of hydrogen (<0·1 mmole), fluoroform (*ca.* 1%), recovered starting materials, and the appropriate alkylbis(trifluoromethyl)phosphine.

(a) *But-1-ene.* Bis(trifluoromethyl)phosphine (11%), but-1-ene (11%), and *n-butylbis(trifluoromethyl)phosphine* (99% on olefin consumed) (Found: C, 32·1; H, 4·3%; *M*, 225. $C_6H_9F_6P$ requires C, 31·9; H, 4·0%; *M*, 226), b.p. 107°/750 mm. Gas chromatography showed only one peak. The ^{1}H n.m.r. spectrum showed complex absorption between τ 7·78 and 9·22. The ^{19}F resonance showed a strong doublet (J_{FP} 71·4 Hz) at −21·9 p.p.m.

(b) trans-*But-2-ene.* Bis(trifluoromethyl)phosphine (11%), a mixture of *cis-* and *trans*-but-2-ene (12%), and 1-*methylpropylbis(trifluoromethyl)phosphine* (99% on olefin consumed) (Found: C, 31·8; H, 4·0%; *M*, 227), b.p. 108°/764 mm. Gas chromatography showed only one peak. The ^{1}H n.m.r. spectrum showed complex absorption between τ 7·39 and 9·11. The ^{19}F resonance at −25·1 p.p.m. showed complicated multiplet structure.

(c) *Tetrafluoroethylene.* Bis(trifluoromethyl)phosphine (75%), tetrafluoroethylene (75%), 1,1,2,2-*tetrafluoroethylbis(trifluoromethyl)phosphine* (98% on olefin consumed) (Found: C, 17·9; H, 0·3%; *M*, 271. $C_4HF_{10}P$ requires C, 17·8; H, 0·4%; *M*, 270), b.p. 61°/755 mm. The ^{1}H n.m.r. spectrum showed a triplet of quartets ($J_{gem\text{-FH}}$ 54·6 Hz; $J_{\alpha\text{FH}} = J_{\text{PH}} = 3·9$ Hz) at τ 4·12. The ^{19}F spectrum had absorptions at −28·6 p.p.m. [6F, d, J_{FP} 77 Hz, $(CF_3)_2P$], +34·1 (2F, d, J_{FP} 56 Hz, $P{\cdot}CF_2$), and +56·1 (2F, dd, J_{FH} 55, J_{FP} 31 Hz, CHF_2), which all showed further fine structure.

An irradiation time of 20 hr. gave hydrogen (0·3 mmole), tetrafluoroethylene (9%), fluoroform (9%), a small amount (<1%) of 1,1,1,2,2,3,3-heptafluoropropane, bis(trifluoromethyl)phosphine (10%), the tertiary phosphine (83% on olefin consumed), and higher-boiling material (0·40 g.).

Tetrafluoroethylene (2·68 g., 26·8 mmoles) and bis(trifluoromethyl)phosphine (4·55 g., 27·0 mmoles) were recovered quantitatively after being kept in the dark at 40° (24 hr.). After 24 hr. at 200°,* the products were fluoroform (0·16 g., 7% on phosphine consumed), tetrafluoroethylene (0·15 g., 5%), perfluorocyclobutane (1·35 g., 53% on olefin consumed), bis(trifluoromethyl)phosphine (1·70 g., 37%), 1,1,2,2-tetrafluoroethylbis(trifluoromethyl)phosphine (3·12 g., 46% on olefin consumed), and a small amount (0·03 g.) of unidentified higher-boiling material.

Preparation of Dimethylphosphine.—Tetramethyldiphosphine disulphide was reduced with lithium aluminium

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* Experiment carried out by Dr. N. F. Wood.

[7] H. Goldwhite, R. N. Haszeldine, and D. G. Rowsell, *J. Chem. Soc.*, 1965, 6875.

hydride in dioxan,[5] and the product was distilled from the reaction mixture and refractionated *in vacuo* to give pure dimethylphosphine (86%) (Found: *M*, 62·1. Calc. for C_2H_7P: *M*, 62·0).

The u.v. spectrum (vapour) showed an inflection at 208 nm. (ε *ca.* 2500) and continued rising absorption to 200 nm. (ε *ca.* 2700). The coupling constants and chemical shifts in the ^1H spectrum were in agreement with those obtained by Roberts and his co-workers.[8]

Since the phosphine readily dissolves tap-grease, it was stored *in vacuo* in sealed ampoules, and manipulation in the vacuum-system was kept to a minimum.

Reaction of Dimethylphosphine with Tetrafluoroethylene.—Dimethylphosphine (1·55 g., 25·0 mmoles) and tetrafluoroethylene (2·5 g., 25·0 mmoles), shaken and irradiated (6 hr.), gave hydrogen (0·001 g., 2%), recovered tetrafluoroethylene (0·48 g., 19%), 1,1,2,2-tetrafluoroethane (0·10 g., 4%), dimethylphosphine (0·21 g., 14%), *dimethyl*-1,1,2,2-*tetrafluoroethylphosphine* (2·27 g., 69% on olefin consumed) (Found: C, 29·5; H, 4·7%; *M*, 162. $C_4H_7F_4P$ requires C, 29·6; H, 4·3%; *M*, 162), b.p. 89°/758 mm., and a high-boiling liquid (*ca.* 1 g.), which was shown by g.l.c. to contain at least four components.

The ^1H n.m.r. spectrum of the tertiary phosphine showed signals at τ 8·81 [6H, d, J_{PH} 3·8 Hz, Me_2P (with further fine structure)] and 4·24 (1H, ttd, CHF_2). The ^{19}F resonance showed signals at +55·2 (2F, ddt, CHF_2) and +45·2 (2F, dq, $CF_2{\cdot}P$).

Dimethylphosphine and tetrafluoroethylene were recovered quantitatively after being kept in the dark at 20° (6 hr.). After 6 hr. at 100° in the dark, dimethylphosphine (1·15 g., 18·5 mmoles) and tetrafluoroethylene (1·85 g., 18·5 mmoles) gave the unchanged phosphine (0·83 g., 72%) and olefin (1·35 g., 73%), hydrogen (<0·1 mmole), 1,1,2,2-tetrafluoroethane (1%), a trace of perfluorocyclobutane, dimethyl-1,1,2,2-tetrafluoroethylphosphine (0·75 g., 92% on olefin consumed), and a small amount (0·05 g.) of higher-boiling material.

Reaction of Dimethylphosphine with Ethylene.—Irradiation of dimethylphosphine (2·08 g., 33·5 mmoles) and ethylene (0·94 g., 33·5 mmoles) in the same way (6 hr.) gave hydrogen (0·003 g., 10%) (Found: *M*, 2·6), ethylene (0·10 g., 11%), dimethylphosphine (0·12 g., 6%), ethyldimethylphosphine (2·15 g., 80% on olefin consumed) (Found: *M*, 89·4. Calc. for $C_4H_{11}P$: *M*, 90·0), b.p. 73°/754 mm. (lit.,[9] b.p. 73°), and higher-boiling material (0·3 g.).

The ^1H n.m.r. spectrum of the tertiary phosphine showed a doublet (J_{PH} 2·8 Hz, Me_2P) at τ 9·07, overlapping a complex region of absorption (EtP) between τ 8·48 and 9·35.

Reaction of Dimethylphosphine with Chlorotrifluoroethylene.—Irradiation of dimethylphosphine (1·77 g., 28·6 mmoles) and chlorotrifluoroethylene (3·33 g., 28·6 mmoles) as before (6 hr.) gave hydrogen (0·6 mmole), chlorotrifluoroethylene (1·00 g., 30%), dimethylphosphine (0·07 g., 4%), 1-chloro-1,2,2-trifluoroethane (0·11 g., 3%), 2-chloro-1,1,2-trifluoroethyldimethylphosphine (2·20 g., 61% on olefin consumed) (Found: C, 27·0; H, 4·0. Calc. for $C_4H_7ClF_3P$: C, 26·9; H, 3·9%), b.p. 110°/410 mm. (lit.[2a] 108°/400 mm.), and higher-boiling material (1·5 g.), shown by g.l.c. to contain at least six components.

The 2-chloro-1,1,2-trifluoroethyldimethylphosphine had i.r. and n.m.r. (^1H and ^{19}F) spectra identical with those of a sample prepared by thermal addition of phosphine to chlorotrifluoroethylene (53% yield) followed by reaction of methylmagnesium iodide with the phosphonous dichloride[2a] (50% yield from the phosphine). The ^1H and ^{19}F n.m.r. spectra are complicated, but have been fully analysed.[10]

Hydrolysis of Alkylbis(trifluoromethyl)phosphines.—Ethylbis(trifluoromethyl)phosphine (0·52 g., 2·6 mmoles) was condensed *in vacuo* into a bulb (500 ml.), dioxan (10 ml.) and aqueous sodium hydroxide (40% w/v; freshly prepared in degassed water) were added, and the bulb was kept at 80° and shaken at ½ hr. intervals (5 hr.), to give fluoroform (0·36 g., 98%), and hydrogen (<0·1 mmole) as the only volatile products. The involatile material was not examined. In the absence of dioxan, fluoroform (16%) was obtained, and ethylbis(trifluoromethyl)phosphine (82%) was recovered after 5 hr. at 80°.

After the same treatment at 80°, n-propyl-, n-butyl-, and 1-methylpropyl-bis(trifluoromethyl)phosphines gave fluoroform (97, 99, and 97% yield respectively) as the only volatile product.

The same treatment of 1,1,2,2-tetrafluoroethylbis(trifluoromethyl)phosphine (0·36 g., 1·33 mmole) (4 hr.) gave fluoroform (0·18 g., 97%) and 1,1,2,2-tetrafluoroethane (0·13 g., 96%).

Hydrolysis of Dimethyl-1,1,2,2-*tetrafluoroethylphosphine.*—Dimethyl-1,1,2,2-tetrafluoroethylphosphine (0·32 g., 2·0 mmoles), sealed *in vacuo* with potassium hydroxide (5 g.) dissolved in ethanol (50 ml.) and shaken at 85° (24 hr.), gave hydrogen (1·92 mmole, 97%) and 1,1,2,2-tetrafluoroethane (0·19 g., 95%). None of the phosphine was recovered.

Dimethyl-1,1,2,2-tetrafluoroethylphosphine (0·23 g., 1·4 mmole), kept with dioxan and 40% aqueous sodium hydroxide at 90° (6 hr.), gave 1,1,2,2-tetrafluoroethane (0·007 g., 5%) and inseparable mixtures of dioxan and the unchanged phosphine.

2-Chloro-1,1,2-trifluoroethyldimethylphosphine (0·56 g., 3·1 mmole), treated in the same way with dioxan and 40% aqueous sodium hydroxide, gave trifluoroethylene (0·035 g., 14%), 1-chloro-1,2,2-trifluoroethane (0·021 g., 6%), and an inseparable mixture of dioxan and the original phosphine.

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[8] G. M. Whitesides, J. L. Beauchamp, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1963, **85**, 2665.

[9] H. D. Kaesz and F. G. A. Stone, *J. Org. Chem.*, 1959, **24**, 635.

[10] J. Dyer, *Proc. Chem. Soc.*, 1963, 273; J. Dyer and J. Lee, *Trans. Faraday Soc.*, 1966, **62**, 257.