199. *Organophosphorus Chemistry. Part I. The Reaction of Phosphine with Fluoro-olefins.*

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Primary polyfluoroalkylphosphines, PH_2R, are readily obtained by photochemical reaction of phosphine with fluoro-olefins. The direction of addition of the $\cdot PH_2$ radical is exclusively to the CF_2 group of $CF_2{:}CFCl$ and to the CH_2 group of $CH_2{:}CF_2$. The olefin C_3F_6 is attacked to the extent of 66% at the CF_2 group and 34% at the CF group. The variation of the direction of radical addition to hexafluoropropene with the electrophilicity or nucleophilicity of the attacking radical is discussed. Primary polyfluoroalkylphosphines, PH_2R, yield the secondary phosphines, PHR_2, when irradiated in presence of a fluoro-olefin. Tetrafluoroethylene reacts with phosphine to give the diphosphinoethane $(CF_2{\cdot}PH_2)_2$ as well as the primary and secondary phosphines $CHF_2{\cdot}CF_2{\cdot}PH_2$, and $(CHF_2{\cdot}CF_2)_2PH$.

A polyfluoroalkylphosphine reacts with chlorine to give the phosphonous dichloride quantitatively. Further reaction with chlorine yields the corresponding phosphorus tetrachloride, pyrolysis of which gives, quantitatively, the polyfluoroalkyl chloride and phosphorus trichloride.

THE study of polyfluoroalkylphosphines has hitherto been restricted by the difficulty of preparing these compounds. Trifluoromethyl- and bistrifluoromethyl-phosphine have been prepared by reduction of the corresponding phosphonous and phosphinous iodides,[1] but yields of individual phosphines are not high. A free-radical reaction between phosphine and fluoro-olefins induced by ultraviolet light has now been found to provide an attractive route to polyfluoroalkylphosphines from readily available starting materials:

$$CF_2{=}CXY + PH_3 \longrightarrow CHXY{\cdot}CF_2{\cdot}PH_2 \text{ and/or } CHF_2{\cdot}CXY{\cdot}PH_2.$$

When a 1 : 1 mixture of tetrafluoroethylene and phosphine was exposed to ultraviolet light, 1,1,2,2-tetrafluoroethylphosphine was produced in 86% yield. 1,1,2,2-Tetrafluoroethane, 1,1,2,2-tetrafluoro-1,2-diphosphino-ethane, and bis-(1,1,2,2-tetrafluoroethyl)phosphine were also produced in small quantities. That bis-(1,1,2,2-tetrafluoroethyl)phosphine arose from further reaction of 1,1,2,2-tetrafluoroethylphosphine with tetrafluoroethylene was established by a separate experiment in which the fluoroalkylphosphine was irradiated in the presence of tetrafluoroethylene. The identity of the product as a secondary phosphine, and not the isomeric product of telomerisation, $H{\cdot}[CF_2{\cdot}CF_2]_2{\cdot}PH_2$, was confirmed by its reaction with chlorine in a 1 : 1 molar ratio to give a phosphinous chloride, $(CHF_2{\cdot}CF_2)_2PCl$ (see below).

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[1] Bennett, Emeléus, and Haszeldine, *J.*, 1953, 1565; 1954, 3598, 3896.

The structure of the diphosphinoethane was confirmed by conversion into, and aqueous alkaline hydrolysis of, the corresponding phosphonous chloride. This yielded 1,1,2,2-tetrafluoroethane and not the isomeric 1,1,1,2-tetrafluoroethane, indicating that the two phosphine groups were on adjacent carbon atoms.

$$H_2P{\cdot}CF_2{\cdot}CF_2{\cdot}PH_2 \xrightarrow{4Cl_2} 4HCl + Cl_2P{\cdot}CF_2{\cdot}CF_2{\cdot}PCl_2 \xrightarrow[H_2O]{OH^-} CHF_2{\cdot}CHF_2$$

The nature of the products, and the reaction conditions, suggest that the reaction involves a radical-chain, *e.g.*:

$$\begin{aligned}
PH_3 &\xrightarrow{h\nu} PH_2{\cdot} + H{\cdot}\\
PH_2{\cdot} + C_2F_4 &\longrightarrow H_2P{\cdot}CF_2{\cdot}CF_2{\cdot}\\
H_2P{\cdot}CF_2{\cdot}CF_2{\cdot} + PH_3 &\longrightarrow H_2P{\cdot}CF_2{\cdot}CHF_2 + PH_2{\cdot}\\
H{\cdot} + C_2F_4 &\longrightarrow CHF_2{\cdot}CF_2{\cdot}\\
CHF_2{\cdot}CF_2{\cdot} + PH_3 &\longrightarrow CHF_2{\cdot}CHF_2 + PH_2{\cdot} \longrightarrow \text{etc.}\\
H_2P{\cdot}CF_2{\cdot}CF_2{\cdot} + PH_2{\cdot} &\longrightarrow H_2P{\cdot}CF_2{\cdot}CF_2{\cdot}PH_2\\
CHF_2{\cdot}CF_2{\cdot}PH_2 &\xrightarrow{h\nu} CHF_2{\cdot}CF_2{\cdot}\dot{P}H \xrightarrow[(2)\ PH_3]{(1)\ C_2F_4} (CHF_2{\cdot}CF_2)_2PH
\end{aligned}$$

However, the yield of the 1,2-diphosphinoethane (10% based on olefin converted) is unusually high for a radical coupling reaction, and alternative pathways for its formation could be involved, *e.g.*, radical displacement on phosphine:

$$H_2P{\cdot}CF_2{\cdot}CF_2{\cdot} + PH_3 \longrightarrow H_2P{\cdot}CF_2{\cdot}CF_2{\cdot}PH_2 + H{\cdot}$$

or radical capture by phosphine followed by an abstraction reaction:

$$H_2P{\cdot}CF_2{\cdot}CF_2{\cdot} + PH_3 \longrightarrow H_2P{\cdot}CF_2{\cdot}CF_2{\cdot}PH_3{\cdot} \xrightarrow{R{\cdot}} H_2P{\cdot}CF_2{\cdot}CF_2{\cdot}PH_2 + RH$$
$$\text{where } R{\cdot} = CHF_2{\cdot}CF_2{\cdot},\ {\cdot}PH_2 \text{ etc.}$$

The diphosphinoethane is not formed by reaction of diphosphine, P_2H_4, with tetrafluoroethylene. When these compounds are mixed and either kept in the dark or irradiated by ultraviolet light, the fluoro-olefin is recovered quantitatively, and the diphosphine decomposes.

It is interesting that irradiation of fluorine-free olefins with phosphine does not produce 1,2-diphosphinoalkanes; irradiation of a mixture of ethylene and phosphine gave ethyl-, diethyl-, and triethyl-phosphine as the only volatile products, thus confirming earlier reports.[2]

Ultraviolet irradiation of a mixture of chlorotrifluoroethylene and phosphine gave a 91% yield of a single 1 : 1 adduct which was a primary phosphine. The structure of this was expected to be $CHFCl{\cdot}CF_2{\cdot}PH_2$ by analogy with known position of attack of other free radicals on this olefin.[3] This structure was established in the following way. Chlorination of the phosphine gave the corresponding phosphonous dichloride, which reacted with a further molecule of chlorine to produce the alkylphosphorus tetrachloride. This compound, on pyrolysis at 250°, gave, quantitatively, an equimolecular mixture of phosphorus trichloride and 1,2-dichloro-1,1,2-trifluoroethane:

$$CHFCl{\cdot}CF_2{\cdot}PH_2 \xrightarrow{2Cl_2} 2HCl + CHFCl{\cdot}CF_2{\cdot}PCl_2 \xrightarrow{Cl_2} CHFCl{\cdot}CF_2{\cdot}PCl_4$$
$$CHFCl{\cdot}CF_2{\cdot}PCl_4 \xrightarrow{250^\circ} CHFCl{\cdot}CF_2Cl + PCl_3$$

The infrared spectrum of the last compound readily distinguished it from the isomeric 1,1-dichloro-1,2,2-trifluoroethane which would have resulted if the phosphine

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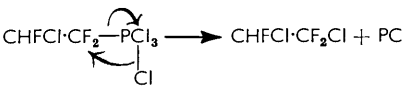
[2] Stiles, Rust, and Vaughan, *J. Amer. Chem. Soc.*, 1952, **74**, 3282.

[3] Haszeldine and Osborne, *J.*, 1956, 61.

$CHF_2\cdot CFCl\cdot PH_2$ had been formed completely or at all by initial attack of the $\cdot PH_2$ radical on the CFCl group of the olefin. Thus, $\cdot PH_2$ radical attack on chlorotrifluoroethylene occurs exclusively on the CF_2 group.

The method described above for the determination of the structure of a polyfluoroalkylphosphine is simple, precise, and unambiguous. The high yields obtained in the elimination, *e.g.*:



$$CHFCl\cdot CF_2{-}PCl_3(Cl) \longrightarrow CHFCl\cdot CF_2Cl + PCl_3$$

are particularly noteworthy.

Irradiation of phosphine and 1,1-difluoroethylene similarly gives the primary phosphine $CHF_2\cdot CH_2\cdot PH_2$ as the major product (74% yield), together with the secondary phosphine $(CHF_2\cdot CH_2)_2PH$. The direction of addition of the $\cdot PH_2$ radical is thus exclusively to the CH_2 group of 1,1-difluoroethylene, and this is in accord with other radical additions, *e.g.*, of Br$\cdot$,[3] $SiCl_3\cdot$,[4] and $CF_3\cdot$.[5]

The structure of the secondary phosphine follows from its synthesis by further reaction of 2,2-difluoroethylphosphine with 1,1-difluoroethylene:

$$CHF_2\cdot CH_2\cdot PH_2 \xrightarrow{h\nu} CHF_2\cdot CH_2\cdot PH\cdot \xrightarrow{CH_2{:}CF_2} CHF_2\cdot CH_2\cdot PH\cdot CH_2\cdot CF_2\cdot$$

$$CHF_2\cdot CH_2\cdot PH\cdot CH_2\cdot CF_2\cdot + PH_3 \longrightarrow (CHF_2\cdot CH_2)_2PH + PH_2\cdot$$

The structure of the primary phosphine was proved by pyrolysis of the corresponding phosphorus tetrabromide to give, quantitatively, phosphorus tribromide and 1-bromo-2,2-difluoroethane, readily distinguishable by infrared spectroscopy from the isomeric 1-bromo-1,1-difluoroethane:

$$CHF_2\cdot CH_2\cdot PH_2 \xrightarrow{Br_2} CHF_2\cdot CH_2\cdot PBr_4 \xrightarrow{\Delta} CHF_2\cdot CH_2Br + PBr_3$$

In this case pyrolysis of the phosphorus tetrachloride was not a suitable method for determining the structure of the phosphine, since the tetrachloride did not decompose cleanly on being heated. Hydrogen chloride was produced and some carbonisation occurred; the reaction was thus comparable with the pyrolysis of unsubstituted alkyl compounds of this type.[6]

A preliminary study of the comparative rates of addition by competitive reaction indicates that reaction of phosphine with tetrafluoroethylene is 5—6 times as fast as reaction with 1,1-difluoroethylene.

Hexafluoropropene reacted sluggishly with phosphine on irradiation with ultraviolet light, to give a 1 : 1-adduct in 97% yield. This was not homogeneous according to gas-chromatography, but the two components revealed by this technique were eluted so nearly together that they could not be separated. The composition of the mixture of phosphines was established by a route similar to that used for the chlorotrifluoroethylene adduct. Thus, conversion of the mixture into the corresponding phosphorus tetrachlorides, and pyrolysis of these, led quantitatively to a mixture containing 66% of 1- and 34% of 2-chloro-1,1,2,3,3,3-hexafluoropropane:

$$C_3F_6 + PH_3 \xrightarrow{h\nu} C_3HF_6\cdot PH_2 \xrightarrow{2Cl_2} C_3HF_6\cdot PCl_2$$

$$C_3HF_6\cdot PCl_2 \xrightarrow{Cl_2} C_3HF_6\cdot PCl_4 \xrightarrow{250^\circ} CF_3\cdot CHF\cdot CF_2Cl\ (66\%) + CF_3\cdot CFCl\cdot CHF_2\ (34\%)$$

The composition of this mixture of propanes was established by gas–liquid chromatography

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[4] Cross, Haszeldine, and Newlands, unpublished work.

[5] Haszeldine and Steele, *J.*, 1954, 923.

[6] Collie and Reynolds, *J.*, 1915, **107**, 367.

and infrared spectroscopy. The inferred composition of the original mixture of phosphines is, therefore, 66% of the compound $CF_3{\cdot}CHF{\cdot}CF_2{\cdot}PH_2$ and 34% of the compound $CF_3{\cdot}CF(PH_2){\cdot}CHF_2$.

The addition of the $\cdot PH_2$ radical to both the terminal CF_2 group and the internal CF group of hexafluoropropene is one further example of two-way addition to this olefin, as shown in the annexed Table.

Radical addition to C_3F_6.

	Attack (%) on starred carbon atom		
Radical attacking	$CF_3{\cdot}CF{:}\overset{*}{C}F_2$	$CF_3{\cdot}\overset{*}{C}F{:}CF_2$	Ref.
$Me_3Si\cdot$	96	4	4
$Me_2SiH\cdot$	95	5	4
$MeS\cdot$	91	9	7
$CF_3\cdot$	85	None detected	8
,,	80	20	9
$MeSiH_2\cdot$	76	24	4
$CF_3{\cdot}CH_2{\cdot}S\cdot$	70	30	7
$PH_2\cdot$	66	34	Present work
$SiH_3\cdot$	60	40	4
$SF_5\cdot$	50	50	10
$CF_3{\cdot}S\cdot$	45	55	7

Direction of Addition During Radical Attack.—The results reported above on the direction of addition of radicals to unsymmetrical olefins will now be considered from two related aspects: (i) the reactivity of the attacking free radical (*i.e.*, the extent to which delocalisation of the lone electron occurs), and the corresponding expected specificity of attack on the olefin; and (ii) the nucleophilic or electrophilic character of the attacking radical, taken in conjunction with the susceptibility towards nucleophilic or electrophilic attack of the olefin being attacked.

Considering (i), one would expect that the more reactive a radical the less discriminating it would be in the position of attack on an olefin. Thus, in the specific case of hexafluoropropene, the more reactive the attacking radical the greater should be the extent of attack on the CF group compared with attack on the CF_2 group (sterically more favoured and leading to the formation of the more stable intermediate radical). Examination of the results in the Table shows that this is not observed. The more reactive the radical (cf. $CF_3{\cdot}S\cdot$ and $CH_3{\cdot}S\cdot$; $SiH_3\cdot$ and $Me_3Si\cdot$) the more discriminating it seems to become. Reactivity in this sense thus has its effect mainly on the *rate* of reaction.

As regards (ii), in any sequence of radicals, the radical most reactive towards an olefin normally susceptible to nucleophilic attack should be the one bearing the most powerful, or the most numerous, electron-releasing substituents, *i.e.*, the most nucleophilic free radical, *e.g.*; $Me_3Si\cdot > Me_2HSi\cdot > MeH_2Si\cdot > H_3Si\cdot$; or $CH_3{\cdot}S\cdot > CF_3{\cdot}CH_2{\cdot}S\cdot > CF_3{\cdot}S\cdot$, $F_5S\cdot$. The reverse order should obtain for attack on an olefin normally susceptible to electrophilic attack. As well as determining rate, the nucleophilic or electrophilic character of the attacking radical could be important in determining the position of attack, particularly when there is not much difference in the relative stabilities of the two radicals that could be produced by attack on the olefin; normally, the difference in stability of these intermediate radicals is sufficient to determine the position of attack, *e.g.*:

$R{\cdot}CH_2{\cdot}CF_2\cdot$ produced rather than $R{\cdot}CF_2{\cdot}CH_2\cdot$

$R{\cdot}CF_2{\cdot}CFCl\cdot$ produced rather than $R{\cdot}CFCl{\cdot}CF_2\cdot$

$R{\cdot}CF_2{\cdot}\dot{C}F{\cdot}CF_3$ produced rather than $RCF(CF_3){\cdot}CF_2\cdot$

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[7] Harris and Stacey, *J. Amer. Chem. Soc.*, 1961, **83**, 840.
[8] Haszeldine, *J.*, 1953, 3559.
[9] Brown and Haszeldine, unpublished work.
[10] Case, Ray, and Roberts, *J.*, 1961, 2070.

where R is the attacking free radical. With hexafluoropropene the difference in stability between $\mathrm{R{\cdot}CF_2{\cdot}\dot{C}F{\cdot}CF_3}$ and $\mathrm{R{\cdot}CF(CF_3){\cdot}CF_2{\cdot}}$ is not great, and the nucleophilic or electrophilic character of R becomes important in determining attack on $\mathrm{CF_2}$ or CF group.

Hexafluoropropene is very sensitive to nucleophilic attack, and as far as is known, nucleophilic attack is exclusively on the $\mathrm{CF_2}$ group. The more nucleophilic the attacking radical, therefore, the more should radical attack be oriented towards the $\mathrm{CF_2}$ group. The series $\mathrm{H_3Si{\cdot}}$, $\mathrm{MeH_2Si{\cdot}}$, $\mathrm{Me_2HSi{\cdot}}$, $\mathrm{Me_3Si{\cdot}}$, and $\mathrm{CF_3{\cdot}S{\cdot}}$, $\mathrm{SF_5{\cdot}}$, $\mathrm{CF_3{\cdot}CH_2{\cdot}S{\cdot}}$, $\mathrm{CH_3{\cdot}S{\cdot}}$, demonstrate this clearly.

The $\mathrm{{\cdot}PH_2}$ radical thus has about the same degree of specificity as the $\mathrm{{\cdot}SiH_3}$ radical towards hexafluoropropene and does not possess a high degree of nucleophilic character.

Chlorination of Polyfluoroalkylphosphines.—Although the chlorination of some alkylphosphines to the corresponding phosphonous dichlorides has been described,[11] no further examples of this reaction have since appeared. The present work shows that excellent yields of polyfluoroalkylphosphonous dichlorides can be obtained simply by sealing equivalent amounts of the polyfluoroalkylphosphine and chlorine in a tube or autoclave at low temperature, and allowing them to warm slowly to room temperature:

$$\mathrm{R{\cdot}PH_2 + 2Cl_2 \longrightarrow RPCl_2 + 2HCl}$$

Under these mild conditions there is no replacement of hydrogen by chlorine in the polyfluoroalkyl group. The following phosphonous dichlorides and phosphinous chlorides, which are colourless liquids which fume in moist air, have been prepared by this method: $\mathrm{CHF_2{\cdot}CF_2{\cdot}PCl_2}$, $\mathrm{CHFCl{\cdot}CF_2{\cdot}PCl_2}$, $\mathrm{CHF_2{\cdot}CH_2{\cdot}PCl_2}$, $\mathrm{(CF_2{\cdot}PCl_2)_2}$, $\mathrm{(CHF_2{\cdot}CF_2)_2PCl}$, $\mathrm{(CHF_2{\cdot}CH_2)_2PCl}$.

An alternative method for preparing polyfluoroalkylphosphonous dichlorides is to heat the polyfluoroalkylphosphines with carbonyl chloride at moderate temperatures and pressures. Under these conditions the dissociation of carbonyl chloride to liberate small amounts of chlorine may provide the effective chlorinating agent:

$$\mathrm{COCl_2 \rightleftharpoons CO + Cl_2}$$

$$\mathrm{CHF_2{\cdot}CF_2{\cdot}PH_2 \xrightarrow{2Cl_2} 2HCl + CHF_2{\cdot}CF_2{\cdot}PCl_2}$$

although a radical chain process can be visualised:

$$\begin{aligned}
\mathrm{COCl_2} &\longrightarrow \mathrm{{\cdot}COCl + Cl{\cdot}}\\
\mathrm{Cl{\cdot} + CHF_2{\cdot}CF_2{\cdot}PH_2} &\longrightarrow \mathrm{CHF_2{\cdot}CF_2{\cdot}PH{\cdot} + HCl}\\
\mathrm{CHF_2{\cdot}CF_2{\cdot}PH{\cdot} + COCl_2} &\longrightarrow \mathrm{CHF_2{\cdot}CF_2{\cdot}PHCl + {\cdot}COCl}\\
\mathrm{{\cdot}COCl} &\longrightarrow \mathrm{CO + Cl{\cdot}}\\
\mathrm{CHF_2{\cdot}CF_2{\cdot}PHCl + Cl{\cdot}} &\longrightarrow \mathrm{CHF_2{\cdot}CF_2{\cdot}PCl{\cdot} + HCl}\\
\mathrm{CHF_2{\cdot}CF_2{\cdot}PCl{\cdot} + COCl_2} &\longrightarrow \mathrm{CHF_2{\cdot}CF_2{\cdot}PCl_2 + {\cdot}COCl} \longrightarrow \text{etc.}
\end{aligned}$$

Carbonyl chloride has been used previously to convert phenylphosphine into phenylphosphonous dichloride [12] and, very recently, for preparing alkylphosphonous dichlorides.[13]

The polyfluoroalkylphosphonous dichlorides are readily hydrolysed, and readily yield tertiary phosphines when treated with Grignard reagents; 2-chloro-1,1,2-trifluoroethyldimethylphosphine was thus obtained:

$$\mathrm{CHFCl{\cdot}CF_2{\cdot}PCl_2 + 2MeMgI \longrightarrow CHFCl{\cdot}CF_2{\cdot}PMe_2}$$

The thermal reaction of phosphine with fluoro-olefins was reported briefly [14] whilst this work was in progress. The yields ranged from 53% for $\mathrm{CHF_2{\cdot}CF_2{\cdot}PH_2}$ and 36% for the 1 : 1 adduct from hexafluoropropene to 1% for the 1 : 1 adduct from 1,1-difluoroethylene. The last compound was characterised only by its mass spectrum and nuclear magnetic

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[11] Walling, U.S.P. 2,437,796; 2,437,798.

[12] Michaelis and Dittler, *Ber.*, 1879, **12**, 338.

[13] Henderson, Buckler, Day, and Grayson, *J. Org. Chem.*, 1961, **26**, 4770.

[14] Parshall, England, and Lindsey, *J. Amer. Chem. Soc.*, 1959, **81**, 4801.

resonance spectrum. The 1 : 1 adduct from hexafluoropropene was considered to be mainly $CF_3{\cdot}CF(PH_2){\cdot}CHF_2$ from nuclear magnetic resonance spectroscopy, in contrast to the chemical proof of structure and isomer ratio described above for the photochemical product. It seems unlikely that the use of heat instead of light would reverse the direction of addition of the $\cdot PH_2$ radical to hexafluoropropene.

EXPERIMENTAL

All materials were manipulated in a conventional high-vacuum apparatus. With the exception of hexafluoropropene, which was prepared by pyrolysis of sodium heptafluorobutyrate, the fluoro-olefins were commercial samples distilled *in vacuo* (to remove inhibitors) before they were used. Infrared spectra and molecular weights were taken as criteria of purity.

Phosphine, prepared by reduction of phosphorus trichloride with lithium alumium hydride or, more conveniently, by heating anhydrous phosphorous acid *in vacuo*, was purified by passing it through concentrated hydrochloric acid and 2N-sodium hydroxide, then over sodium hydroxide pellets and phosphorus pentoxide.

1,1,2,2-*Tetrafluoroethylphosphine.*—Phosphine (1·34 g., 39·5 mmoles) and tetrafluoroethylene (3·95 g., 39·5 mmoles), sealed in a 380-ml. silica tube (initial pressure 5 atm.), were irradiated for 160 hr. by a Hanovia U.V.S. 500 lamp. The products were fractionated *in vacuo*, to give unchanged phosphine (0·34 g., 10·1 mmoles, 26%), tetrafluoroethylene (1·06 g., 10·6 mmoles, 27%), and 1,1,2,2-*tetrafluoroethylphosphine* (3·09 g., 24·9 mmoles, 86% based on olefin consumed) (Found: C, 18·2; H, 2·0%; *M*, 134. $C_2H_3F_4P$ requires C, 17·9; H, 2·2%; *M*, 134). The phosphine is a colourless liquid, distilling at 18·8—20·2°/735 mm.

Its b. p., determined by extrapolation of the vapour-pressure curve, is 20·7°, its latent heat of vaporisation is 6450 cal./mole, and Trouton's constant is 21·9.

Larger-scale syntheses of tetrafluoroethylphosphine were carried out in a 20-l. bulb in which an ultraviolet lamp (Hanovia U.V.S. 500) was suspended. Phosphine (11·75 g., 0·346 mole) and tetrafluoroethylene (34·6 g., 0·346 mole) were placed in the bulb at an initial pressure of 700 mm. at 20° and irradiated for 19 hr. The unchanged reactants obtained on fractionation were returned to the bulb and irradiated for a further 19 hr. Distillation gave 1,1,2,2-tetrafluoroethylphosphine (19·2 g., 0·143 mole, 84% based on olefin converted) together with phosphine (5·85 g., 0·172 mole, 50%), tetrafluoroethylene (17·6 g., 0·176 mole, 51%), and higher-boiling products (3·2 g.).

With these larger-scale syntheses it was possible to investigate the by-products of the reaction: (i) 1,1,2,2-tetrafluoroethane (5% yield based on olefin consumed) (Found: *M*, 101; Calc. for $C_2H_2F_4$: *M*, 102), b. p. −21° to −18°/760 mm., identified by its infrared spectrum; (ii) 1,2-*diphosphinotetrafluoroethane* (9% yield based on olefin consumed) (Found: C, 14·6; H, 2·3%; *M*, 167. $C_2H_4F_4P_2$ requires C, 14·5; H, 2·4%; *M*, 166), b. p. 74·5—76°/755 mm.; and (iii) *bis*-(1,1,2,2-*tetrafluoroethyl*)*phosphine* (2% yield based on olefin consumed) (Found: C, 20·6; H, 1·5%; *M*, 231. $C_4H_3F_8P$ requires C, 20·5; H, 1·3%; *M*, 234), b. p. 92—93°/756 mm.

Chlorinations of bis-(1,1,2,2-tetrafluoroethyl)phosphine to bis-(1,1,2,2-tetrafluoroethyl)-phosphinous chloride and of 1,2-diphosphinotetrafluoroethane to tetrafluoroethyl-1,2-diphosphonous dichloride are described below.

Tetrafluoroethyl-1,2-diphosphonous dichloride (0·57 g., 1·89 mmoles) was treated in a bulb (300 ml.) with an excess of 40% aqueous sodium hydroxide. After 2 hr. at room temperature the volatile products were fractionated, to yield 1,1,2,2-tetrafluoroethane (0·19 g., 1·82 mmoles, 96%) (Found: *M*, 102. Calc. for $C_2H_2F_4$: *M*, 102), identified by its infrared spectrum.

Bis-(1,1,2,2-*tetrafluoroethyl*)*phosphine from* 1,1,2,2-*Tetrafluoroethylphosphine and Tetrafluoroethylene.*—1,1,2,2-Tetrafluoroethylphosphine (3·40 g., 25·4 mmoles) and tetrafluoroethylene (2·42 g., 24·2 mmoles), sealed in a 350-ml. silica tube (initial pressure 3 atm.), were irradiated for 85 hr. by a Hanovia U.V.S. 500 lamp. The products were fractionated *in vacuo*, to give unchanged tetrafluoroethylene (0·98 g., 9·8 mmoles, 41%), 1,1,2,2-tetrafluoroethylphosphine (1·45 g., 10·8 mmoles; 43%), and bis-(1,1,2,2-tetrafluoroethyl)phosphine (2·78 g., 11·9 mmoles, 81% based on primary phosphine consumed), b. p. 91—93°/760 mm., shown by infrared spectroscopy to be identical with the material obtained as above.

Irradiation of Tetrafluoroethylene with Diphosphine (Experiments carried out by Mr. A.

KERRY).—Tetrafluoroethylene (3·04 g., 30·4 mmoles) and diphosphine [15] (2·70 g., 41 mmoles), sealed in a 350-ml. silica tube, were irradiated for 12 hr. by a Hanovia U.V.S. 250 lamp. The tube walls became heavily coated with a yellow solid. The products were fractionated *in vacuo* to give unchanged tetrafluoroethylene (3·04 g., 30·4 mmoles, 100%) and phosphine (1·36 g., 40 mmoles, 97%). No trace of 1,2-diphosphinotetrafluoroethane was detected. Thus even mild photolysis is sufficient to decompose diphosphine into phosphine; ultraviolet light of the intensity used is insufficient to initiate addition of phosphine to tetrafluoroethylene to any extent during the reaction time employed. A similar experiment in which a mixture of diphosphine and tetrafluoroethylene was left in the dark for 24 hr. also gave only unchanged tetrafluoroethylene and phosphine.

Irradiation of Ethylene with Phosphine.—Ethylene (0·97 g., 34·8 mmoles) and phosphine (1·28 g., 37·5 mmoles), sealed in a 350-ml. silica tube (initial pressure 6 atm.), were irradiated for 250 hr. by a Hanovia U.V.S. 500 lamp. The products were fractionated *in vacuo*, to give unchanged ethylene (0·12 g., 4·4 mmoles, 13%), phosphine (0·78 g., 23·0 mmoles, 61%), and ethylphosphine (0·09 g., 1·52 mmoles, 5%) (Found: *M*, 62. Calc. for C_2H_7P: *M*, 62), diethylphosphine (0·20 g., 2·25 mmoles, 7%), b. p. 86—87°/763 mm., and triethylphosphine (0·92 g., 7·8 mmoles, 25%), b. p. 127—128°/763 mm. A light brown deposit was left in the tube.

2-*Chloro*-1,1,2-*trifluoroethylphosphine.*—Phosphine (1·33 g., 39·0 mmoles) and chlorotrifluoroethylene (4·55 g., 39·0 mmoles), sealed in a 350-ml. silica tube and irradiated for 12 hr., gave 2-*chloro*-1,1,2-*trifluoroethylphosphine* (2·0 g., 13·2 mmoles, 91% based on olefin consumed) (Found: C, 16·0; H, 2·0%; *M*, 151. $C_2H_3ClF_3P$ requires C, 16·0; H, 2·0%; *M*, 151), b. p. 66—67°/746 mm., unchanged phosphine (0·67 g., 19·6 mmoles, 50%), chlorotrifluoroethylene (2·84 g., 24·4 mmoles, 63%), and some higher-boiling materials which were not further investigated. Gas–liquid chromatography of the 1 : 1 adduct on 2-m. columns with stationary phases of silicone oil, a polychlorotrifluoroethylene oil, or dinonyl phthalate failed to show more than one component.

Synthesis of 2-chloro-1,1,2-trifluoroethylphosphine could also be carried out conveniently in the 20-l. bulb described above for the synthesis of 1,1,2,2-tetrafluoroethylphosphine. Chlorotrifluoroethylene (52·5 g., 0·45 mole) and phosphine (15·3 g., 0·45 mole) were irradiated in the bulb for 55 hr. The volatile products were distilled *in vacuo*, to give 2-chloro-1,1,2-trifluoroethylphosphine (20·3 g., 0·13 moles, 89%), together with unchanged phosphine (9·85 g., 0·29 mole, 64%) and chlorotrifluoroethylene (35·0 g., 0·30 mole, 67%).

Pyrolysis of 2-*Chloro*-1,1,2-*trifluoroethylphosphorus Tetrachloride.*—2-Chloro-1,1,2-trifluoroethylphosphine (1·58 g., 10·5 mmoles) and chlorine (2·23 g., 31·3 mmoles) were sealed together at −183° in a 265-ml. silica tube. The tube was allowed to warm slowly to room temperature, then opened to remove hydrogen chloride (0·75 g., 20·7 mmoles, 99%), leaving a colourless involatile liquid. The tube was resealed and heated at 250° for 1 hr. The products were fractionated *in vacuo*, to yield phosphorus trichloride (1·38 g., 10·1 mmoles, 96%) and 1,2-dichloro-1,1,2-trifluoroethane (1·56 g., 10·3 mmoles, 98%) (Found: *M*, 153. Calc. for $C_2HCl_2F_3$: *M*, 153) shown by infrared spectroscopy to be identical with an authentic sample of this compound.

2,2-*Difluoroethylphosphine.*—Phosphine (1·24 g., 42·0 mmoles) and 1,1-difluoroethylene (2·68 g., 41·9 mmoles), sealed together in a 380-ml. silica tube and irradiated for 200 hr., yielded 2,2-*difluoroethylphosphine* (1·76 g., 17·9 mmoles, 74% based on olefin consumed) (Found: C, 24·3; H, 5·1%; *M*, 97·5. $C_2H_5F_2P$ requires C, 24·5; H, 5·1%; *M*, 98·0), b. p. 52—53°/758 mm. Unchanged phosphine (0·60 g., 17·7 mmoles, 42%) and 1,1-difluoroethylene (1·12 g., 17·6 mmoles, 42%) were also recovered from the reaction mixture together with small amounts of higher-boiling liquids.

2,2-Difluoroethylphosphine (0·45 g., 4·6 mmoles) and bromine (2·24 g., 14·0 mmoles) were sealed together in a silica tube (265 ml.) at −130° and allowed to warm slowly to room temperature. Hydrogen bromide (0·71 g., 8·9 mmoles) was removed and the residual orange solid was heated gently with a free flame. The volatile products of this thermal decomposition were fractionated *in vacuo*, to yield 1-bromo-2,2-difluoroethane (0·65 g., 4·5 mmoles, 98%) (Found: *M*, 144. Calc. for $C_2H_3BrF_2$: *M*, 145), identified by its infrared spectrum which was identical with that of an authentic sample of this compound prepared by free-radical addition of hydrogen bromide to 1,1-difluoroethylene.[3]

Bis-(2,2-*difluoroethyl*)*phosphine.*—(i) *By irradiation of phosphine and* 1,1-*difluoroethylene.*

[15] Evers and Street, *J. Amer. Chem. Soc.*, 1956, **78**, 5726.

The higher-boiling liquids from a number of experiments of the type described above were combined and distilled to yield *bis-*(2,2-*difluoroethyl*)*phosphine* (~28% yield based on olefin consumed) (Found: C, 29·8; H, 4·2. $C_4H_7F_4P$ requires C, 29·6; H, 4·3%), b. p. 108—109°/226 mm.

(ii) *From* 2,2-*difluoroethylphosphine and* 1,1-*difluoroethylene.* 2,2-Difluoroethylphosphine (0·93 g., 9·4 mmoles) and 1,1-difluoroethylene (1·83 g., 29·0 mmoles) were sealed in a silica tube (380 ml.) and irradiated for 125 hr. Fractionation gave bis-(2,2-difluoroethyl)phosphine (1·40 g., 8·6 mmoles, 92% based on the primary phosphine consumed), b. p. 109—110°/235 mm., shown by infrared spectroscopy to be identical with the material obtained as in (i). Unchanged 2,2-difluoroethylphosphine (0·04 g., 0·36 mmole, 4%) and 1,1-difluoroethylene (1·19 g., 18·5 mmoles, 64%) were also recovered.

Competition between Tetrafluoroethylene and 1,1-*Difluoroethylene for the* $\cdot PH_2$ *Radical.*—Phosphine (0·58 g., 17·0 mmoles), tetrafluoroethylene (1·72 g., 17·2 mmoles), and 1,1-difluoroethylene (1·90 g., 17·1 mmoles) were sealed in a silica tube (380 ml.), and irradiated for 1 hr. The contents of the tube were fractionated *in vacuo*. Infrared spectroscopy showed that separation of the primary phosphines from unchanged phosphine and tetrafluoroethylene was complete. Gas–liquid chromatography of the primary phosphines (dinonyl phthalate column) also failed to show any material other than the two primary phosphines; as these materials were eluted very nearly together it was not possible to analyse the mixture precisely by gas–liquid chromatography. The molecular weight of the mixture of phosphines (*M*, 128·6) corresponds to a mixture of 85% of 1,1,2,2-tetrafluoroethylphosphine and 15% of 2,2-difluoroethylphosphine. A second experiment gave the same ratio of the two compounds.

Hexafluoropropylphosphine.—Phosphine (1·73 g., 51·0 mmoles) and hexafluoropropene (7·60 g., 50·7 mmoles), sealed in a silica tube (380 ml.) and irradiated for 350 hr., yielded hexafluoropropylphosphine (1·61 g., 8·7 mmoles, 97% based on olefin consumed) (Found: C, 19·8; H, 1·6%; *M*, 183. Calc. for $C_3H_3F_6P$: C, 19·6; H, 1·6%; *M*, 184), b. p. 47—48°/768 mm., phosphine (1·36 g., 39·9 mmoles, 78%), and hexafluoropropene (6·06 g., 40·4 mmoles, 79%).

Gas–liquid chromatography of the hexafluoropropylphosphine at room temperature on a 2-m. column with silicone oil as the stationary phase showed two overlapping peaks which could not be completely separated by lengthening the column or by use of other stationary phases.

The structures of the two components were elucidated by pyrolysis of the corresponding phosphorus tetrachlorides. Hexafluoropropylphosphine (1·38 g., 7·5 mmoles) and chlorine (1·60 g., 22·5 mmoles) were sealed together in a silica tube (380 ml.) at −183° and allowed to warm slowly to room temperature. Hydrogen chloride (0·55 g., 15·0 mmoles, 100%) was removed, and the residual colourless hexafluoropropylphosphorus tetrachloride mixture (Found: Cl, 43·8. Calc. for $C_3HCl_4F_6P$: Cl, 43·8%) was heated at 250° for 1 hr., to yield phosphorus trichloride (0·92 g., 6·7 mmoles, 89%) and a mixture of 2- and 1-chloro-1,1,2,3,3,3-hexafluoropropane (total wt. 1·39 g., 7·5 mmoles, 100%) (Found: *M*, 185. Calc. for C_3HClF_6: *M*, 186·5). Infrared spectroscopy and gas–liquid chromatography (3-m. column with dinonyl phthalate stationary phase) showed this mixture to contain 66% of the 1-chloro- and 34% of the 2-chloropropane.

Conversion of Phosphines into Chlorides.—2,2-Difluoroethylphosphine (3·78 g., 38·6 mmoles) and chlorine (5·40 g., 76·0 mmoles) were condensed, at two separate levels, into a "Dreadnought" tube (400 ml.), which was allowed to warm very slowly to room temperature during 12 hr. Fractionation *in vacuo* gave hydrogen chloride (2·76 g., 75·5 mmoles, 98%) and 2,2-*difluoroethyl phosphonous dichloride* (5·50 g., 33·0 mmoles, 85%) (Found: C, 14·5; H, 1·9; *M*, 166. $C_2H_3ClF_2P_2$ requires C, 14·6; H. 1·8%; *M*, 167), b. p. 116—117°/764 mm. the chlorination may be dangerous on a large scale.

The following were similarly prepared from the corresponding phosphines:

1,1,2,2-*Tetrafluoroethylphosphonous dichloride*, b. p. 87—88°/773 mm. (Found: C, 11·8; H, 0·7%; *M*, 204. $C_2HCl_2F_4P$ requires C, 11·8; H, 0·5%; *M*, 203).

2-*Chloro*-1,1,2-*trifluoroethylphosphonous dichloride*, b. p. 128—130°/780 mm. (Found: C, 11·1; H, 0·6. $C_2HCl_3F_3P$ requires C, 11·0; H, 0·5%).

Bis-(2,2-*difluoroethyl*)*phosphinous chloride*, b. p. 120—122°/180 mm. (Found: C, 24·7; H, 3·0. $C_4H_6ClF_4P$ requires C, 24·5; H, 3·1%).

Bis-(1,1,2,2-*tetrafluoroethyl*)*phosphinous chloride*, b. p. 164—166°/755 mm. (Found: C, 18·1; H, 0·6. $C_4H_2ClF_8P$ requires C, 17·9; H, 0·7%).

Tetrafluoroethyl-1,2-*diphosphonous dichloride*, b. p. 178—180°/758 mm. (Found: C, 8·3; Cl, 46·9. $C_2Cl_4F_4P_2$ requires C, 8·0; Cl, 46·7%).

2-*Chloro*-1,1,2-*trifluoroethyldimethylphosphine*.—Methylmagnesium iodide [from methyl iodide (54·0 g., 0·38 mole), magnesium (9·1 g., 0·38 g.-atom), and sodium-dried diethyl ether (120 ml.)] was heated under reflux, then 2-chloro-1,1,2-trifluoroethylphosphonous dichloride (15·5 g., 0·07 mole) in diethyl ether (40 ml.) was added at such a rate that reflux was maintained. The mixture was stirred and heated for 30 min. then cooled and hydrolysed with 2N-sulphuric acid (135 ml.). The ethereal layer was separated, washed with water (2 × 50 ml.), dried ($MgSO_4$) and distilled, to yield 2-*chloro*-1,1,2-*trifluoroethyldimethylphosphine* (8·0 g., 0·045 mole, 64%) (Found: C, 26·8; H, 3·8. $C_4H_7ClF_3P$ requires C, 26·9; H, 3·9%), b. p. 108°/400 mm.

Reaction between Carbonyl Chloride and 1,1,2,2-*Tetrafluoroethylphosphine*.—Carbonyl chloride (3·92 g., 39·6 mmoles) and 1,1,2,2-tetrafluoroethylphosphine (5·31 g., 39·6 mmoles) in a stainless-steel autoclave (89 ml.) were heated at 155—160° for 24 hr. The volatile products were distilled *in vacuo*, to give unchanged tetrafluoroethylphosphine (3·16 g., 24·6 mmoles, 60%), carbonyl chloride (1·20 g., 12·1 mmoles, 31%), carbon monoxide (0·78 g., 27·5 mmoles, 100% based on carbonyl chloride consumed), hydrogen chloride (1·01 g., 27·5 mmoles, 100%), and 1,1,2,2-tetrafluoroethylphosphonous dichloride (2·95 g., 14·5 mmoles, 97%), b. p. 87·5—89°/770 mm.

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