115. *Organophosphorus Chemistry. Part II.* Phospha-alkenes as Intermediates in Hydrolysis.*

By G. M. Burch, H. Goldwhite, and R. N. Haszeldine.

When a phosphine containing the group $>CF{\cdot}PH{-}$ is treated with aqueous base, loss of hydrogen fluoride occurs: a phospha-alkene ($>C{=}P{-}$) is postulated as a reactive intermediate. A polyfluoroalkylphosphine thus ultimately yields, after cleavage of a carbon–phosphorus bond, products in which halogen has been eliminated from both α- and β-carbon atoms.

Alkaline hydrolysis of polyfluoroalkylphosphonous dichlorides leads to the corresponding polyfluoroalkane, which is mixed with an alkene if the polyfluoroalkane is readily dehydrohalogenated. 2,2-Difluoroethylphosphonous dichloride gives acetylene under these conditions. Neutral hydrolysis of a polyfluoroalkylphosphonous dichloride, followed by oxidation, gives the corresponding polyfluoroalkylphosphonic acid.

The bond between carbon and phosphorus is generally regarded as stable to hydrolysis, but in perfluoroalkyl derivatives of phosphorus the strongly electron-withdrawing organic group makes the phosphorus atom susceptible to nucleophilic attack, and easy carbon–phosphorus bond fission results, *e.g.*: [1]

$$CF_3{\cdot}PI_2 \xrightarrow{\text{Aq. NaOH}} CHF_3\ (100\%)$$

Carbon–phosphorus bond fission has now been found when polyfluoroalkyl derivatives of phosphorus, $R{\cdot}CFX{\cdot}CF_2{\cdot}PY_2$, are subjected to aqueous hydrolysis, but the nature of the products depends on whether Y is hydrogen or halogen; if fluorine is not present on the α-carbon of the alkyl group, carbon–phosphorus fission does not occur when Y = H.

Hydrolysis of Polyfluoroalkylphosphonous Dichlorides.—Polyfluoroalkylphosphonous dichlorides, $R{\cdot}CFX{\cdot}CF_2{\cdot}PCl_2$ (X = H, F, or Cl), in which there is a difluoromethylene group adjacent to phosphorus, are hydrolysed analogously to trifluoromethylphosphonous

---

* Part I, *J.*, 1963, 1083.

[1] Bennett, Emeléus, and Haszeldine, *J.*, 1953, 1565.

dihalides,[1] giving polyfluoroalkanes, or mixtures of polyfluoro-alkanes and -alkenes if the alkane is susceptible to dehydrohalogenation. Thus, 1,1,2,2-tetrafluoroethylphosphonous dichloride gives, on treatment with 40% aqueous sodium hydroxide, 94% of the theoretical amount of 1,1,2,2-tetrafluoroethane:

$$CHF_2\cdot CF_2\cdot PCl_2 \xrightarrow{\text{Aq. NaOH}} CHF_2\cdot CF_2\cdot P(OH)_2 \xrightarrow{\text{Aq. NaOH}} CHF_2\cdot CHF_2$$

Similarly hexafluoropropylphosphonous dichloride [a 2 : 1 mixture of the compounds, $CF_3\cdot CHF\cdot CF_2\cdot PCl_2$ and $CF_3\cdot CF(PCl_2)\cdot CHF_2$; see Part I] gives a nearly quantitative yield of the polyfluoroalkane, $CF_3\cdot CHF\cdot CHF_2$; a 96% yield of 1,1,2,2-tetrafluoroethane is obtained from the compound $(CF_2\cdot PCl_2)_2$.

2-Chloro-1,1,2-trifluoroethylphosphonous dichloride, however, gives a mixture of 2-chloro-1,1,2-trifluoroethane (26%) and trifluoroethylene (73%). A separate experiment showed that the olefin can arise by dehydrochlorination of the chlorofluoroalkane under the hydrolysis conditions used:

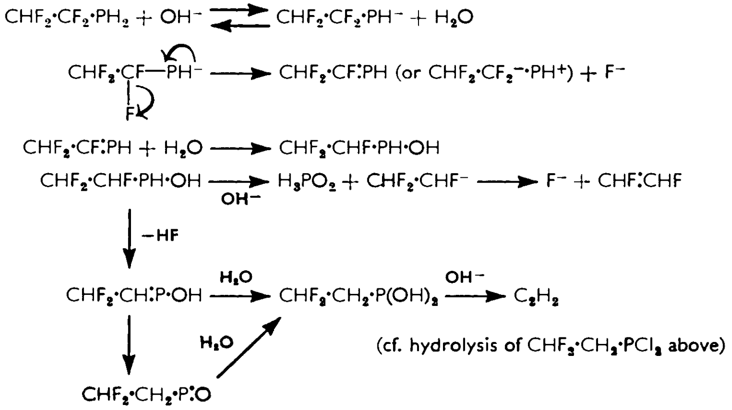
$$CHFCl\cdot CF_2\cdot PCl_2 \xrightarrow{\text{Aq. NaOH}} CHFCl\cdot CHF_2 \xrightarrow{\text{Aq. NaOH}} CHF{:}CF_2$$

The aqueous alkaline hydrolysis of 2,2-difluoroethylphosphonous dichloride under similar conditions gives a quantitative yield of acetylene. This result is surprising at first sight, since both the alkane, $CHF_2\cdot CH_3$, and the olefin, $CH_2{:}CHF$, which might have been expected, are stable to aqueous base under the conditions used, and would easily have been detected had they been produced. Dehydrofluorination of the 2,2-difluoroethyl group before cleavage of the carbon–phosphorus bond in the phosphonous acid thus probably occurs; the fluorovinyl ion so produced loses fluoride ion:

$$CHF_2\cdot CH_2\cdot PCl_2 \longrightarrow CHF_2\cdot CH_2\cdot P(OH)_2 \xrightarrow{\text{Aq. NaOH}} CHF{:}CH\cdot P(OH)_2 \xrightarrow{OH^-} H_3PO_3 + CHF{:}CH^- \longrightarrow F^- + C_2H_2$$

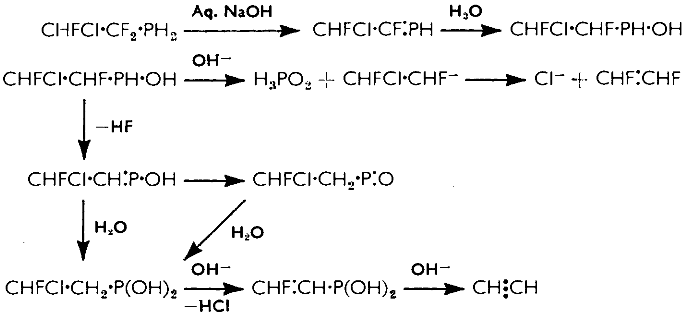
Hydrolysis of Polyfluoroalkylphosphines.—Phosphines of type $R\cdot CFX\cdot CF_2\cdot PH_2$ are stable to neutral or acidic aqueous solutions, but react rapidly with aqueous base. The nature of the products suggests strongly that the first step is dehydrofluorination to produce a phospha-alkene: $>CF\cdot PH_2 \longrightarrow >C{:}PH$. Phospha-alkenes, that can be postulated as existing in forms $>C{=}P-$ or $>C^-\cdot P^+-$, here suggested as intermediates, differ from the well-known phosphinomethylenes in that they contain tervalent phosphorus but, as later papers in this series will show, they are highly reactive entities and valuable intermediates in synthesis. The polarisation, $>C^-\cdot P^+-$, which might be expected from the relative electronegativities of carbon and phosphorus, is consistent with the reactions of this type of intermediate.

The volatile products of hydrolysis of 1,1,2,2-tetrafluoroethylphosphine with 40% aqueous sodium hydroxide are 1,2-difluoroethylene (95%), acetylene (5%), and hydrogen. Formation of the major product has thus involved removal of fluoride ion from both α- and β-positions of the original polyfluoroalkyl group, as shown in the annexed scheme.



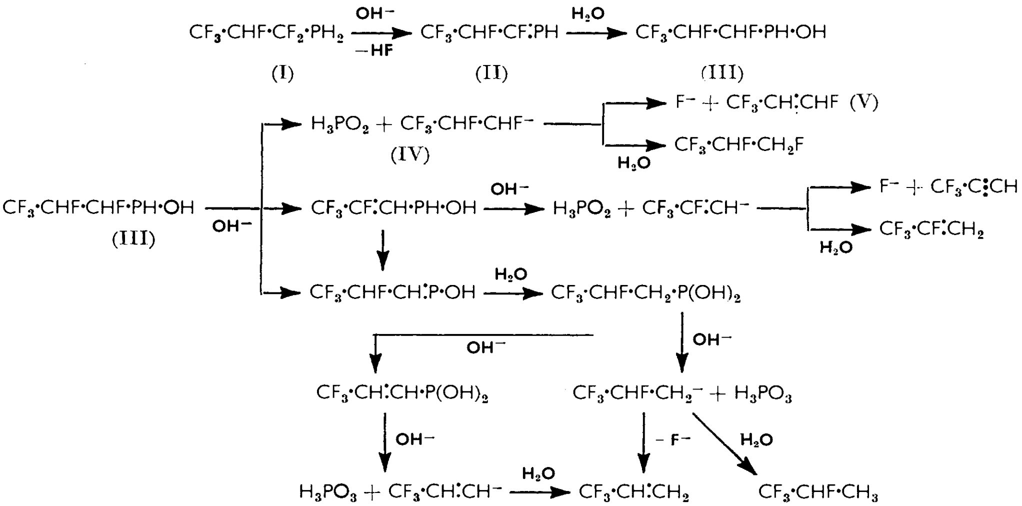
The hydrogen produced arises from the reducing action of hypophosphorous acid (H_3PO_2) on the basic solution; this was demonstrated by a control experiment.

The products of basic hydrolysis of other polyfluoroalkylphosphines can be accounted for by similar schemes. 2-Chloro-1,1,2-trifluoroethylphosphine gives 1,2-difluoroethylene (73%), acetylene (5%), and hydrogen:



(cf. hydrolysis of $CHF_2{\cdot}CH_2{\cdot}PCl_2$)

By analogy, the reaction of the mixture of hexafluoropropylphosphines (see above) with aqueous base might proceed as illustrated for the isomer $CF_3{\cdot}CHF{\cdot}CF_2{\cdot}PH_2$. However, since hydrogen is again a product, hypophosphorous acid must be formed rather than phosphorous acid, and, since the only olefin formed (in quantitative yield) is 1,3,3,3-tetrafluoropropene, reactions leading to the formation of products $CF_3{\cdot}CHF{\cdot}CH_2F$, $CF_3{\cdot}CH_2{\cdot}CH_2F$, $CF_3{\cdot}CF{:}CH_2$, $CF_3{\cdot}CHF{\cdot}CH_3$, $CF_3{\cdot}CH{:}CH_2$, or $CF_3{\cdot}C{:}CH$, can be eliminated. The most important reactions are thus (I) ⟶ (II) ⟶ (III) ⟶ H_3PO_2 + (IV) ⟶ (V), with analogous reactions for the isomer.

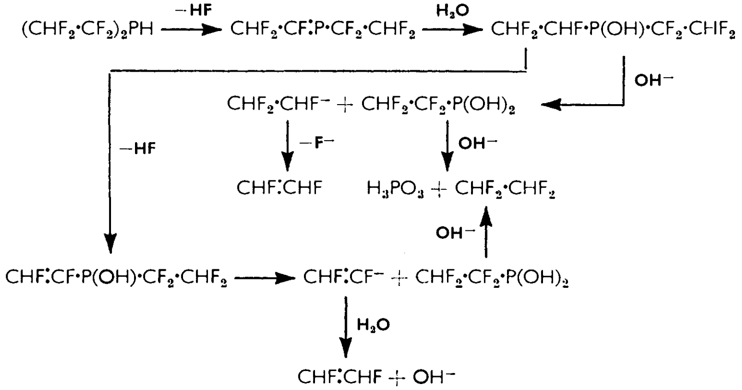


The olefinic product was identified by comparison of its infrared spectrum with that of a known specimen; the intense carbon–carbon double-bond stretching frequency at 1695 cm.$^{-1}$ indicates the presence of the $-CH{:}CHF$ group [2] and distinguishes the compound from the isomer $CHF_2{\cdot}CH{:}CF_2$ which would have intense absorption at about 1780 cm.$^{-1}$ due to its double bond.[3]

[2] Haszeldine and Steele, *J.*, 1953, 1199.
[3] Haszeldine and Steele, *J.*, 1954, 923.

It is interesting that in the analogous reaction scheme for the isomer $CF_3{\cdot}CF(Ph_2){\cdot}CHF_2$ the secondary carbanion, $CF_3{\cdot}CH^-{\cdot}CHF_2$, must eliminate fluoride ion exclusively from the difluoromethyl group since only the olefin $CF_3{\cdot}CH{:}CHF$ is formed.

The hydrolysis of bis-1,1,2,2-tetrafluoroethylphosphine gave, quantitatively, a 1 : 1 mixture of 1,1,2,2-tetrafluoroethane and 1,2-difluoroethylene, again *via* a phospha-alkene:



The fact that the alkane and the alkene are each obtained in 50% yield shows that only one of the two tetrafluoroethyl groups loses two fluorines to give 1,2-difluoroethylene, but it is not yet possible to distinguish between the alternative pathways leading from the intermediate $CHF_2{\cdot}CHF{\cdot}P(OH){\cdot}CF_2{\cdot}CHF_2$. The absence of hydrogen as product of this reaction is in accord with the above mechanism, since the phosphorous acid produced does not reduce basic solutions.

Aqueous alkaline hydrolysis of the phosphinous chloride $(CHF_2{\cdot}CF_2)_2PCl$ gave 1,1,2,2-tetrafluoroethane in 97% yield.

In contrast with the preceding observations, 2,2-difluoroethylphosphine is stable to 40% aqueous sodium hydroxide at room temperature. This phosphine, $CHF_2{\cdot}CH_2{\cdot}PH_2$, carries no halogen atom on the carbon atom adjacent to the phosphine group and consequently the initial formation of the phospha-alkene cannot occur. 2,2-Difluoroethylphosphine is also insoluble in 40% aqueous sodium hydroxide and so cannot undergo hydrolysis in the way suggested above for 2,2-difluoroethylphosphonous dichloride, which rapidly dissolves in aqueous sodium hydroxide and so can be attacked further by it.

Polyfluoroalkylphosphonic Acids.—The neutral hydrolyses of the phosphonous dichlorides, $CHF_2{\cdot}CF_2{\cdot}PCl_2$, $CHFCl{\cdot}CF_2{\cdot}PCl_2$, $CHF_2{\cdot}CH_2{\cdot}PCl_2$, and $Cl_2P{\cdot}CF_2{\cdot}CF_2{\cdot}PCl_2$, gave the corresponding phosphonous acids, which were not isolated in this form but were oxidised by neutral hydrogen peroxide to the polyfluoroalkyl phosphonic acids:

$$R_F{\cdot}PCl_2 \xrightarrow{H_2O} R_F{\cdot}P(OH)_2 \xrightarrow{H_2O_2} R_F{\cdot}PO(OH)_2$$

These strong acids, most of which are hygroscopic though crystalline, were characterised by analysis, by titration, and as salts with organic bases. The dissociation constants of the acids, and others included for comparison, are given in the annexed Table.

Dissociation constants of phosphonic acids, $R{\cdot}PO(OH)_2$.

R	K_1	K_2	Ref.
CF_3	$6{\cdot}8 \times 10^{-2}$	$1{\cdot}2 \times 10^{-4}$	*a*
$n\text{-}C_3F_7$	$1{\cdot}3 \times 10^{-1}$	$1{\cdot}1 \times 10^{-4}$	*b*
$CHF_2{\cdot}CF_2$	$2{\cdot}5 \times 10^{-2}$	$2{\cdot}2 \times 10^{-5}$	*c*
$CHFCl{\cdot}CF_2$	$1{\cdot}0 \times 10^{-2}$	$2{\cdot}1 \times 10^{-5}$	*c*
$CHF_2{\cdot}CH_2$	$1{\cdot}3 \times 10^{-2}$	$1{\cdot}7 \times 10^{-7}$	*c*
C_2H_5	$3{\cdot}6 \times 10^{-3}$	$1{\cdot}4 \times 10^{-8}$	*d*

Refs.: (*a*) Bennett, Emeléus, and Haszeldine, *J.*, 1954, 3598. (*b*) Emeléus and Smith, *J.*, 1959, 375. (*c*) Present work. (*d*) Crofts and Kosolapoff, *J. Amer. Chem. Soc.*, 1953, **75**, 3379.

EXPERIMENTAL

Polyfluoroalkyl-phosphines and -phosphonous dichlorides were prepared by published methods (Part I). Vinyl fluoride, 1,1-difluoroethane, and 2-chloro-1,1,2-trifluoroethane were prepared by standard methods. Volatile products were identified by their infrared spectra, gas-liquid chromatography characteristics, and molecular weights.

Hydrolyses of Polyfluoroalkylphosphonous Dichlorides.—(i) 1,1,2,2-*Tetrafluoroethylphosphonous dichloride.* This compound (0·51 g., 2·48 mmoles) was condensed into a finger attached to an evacuated 300-ml. bulb. 40% Sodium hydroxide solution (10 ml., 100 mmoles; freshly prepared in boiled-out water) was added slowly through the tap attached to the bulb, and an exothermic reaction occurred. The bulb was left at room temperature for 2 hr. and the volatile products of reaction were then fractionated *in vacuo* to yield 1,1,2,2-tetrafluoroethane (0·24 g., 2·32 mmoles, 94%) (Found: *M*, 102. Calc. for $C_2H_2F_4$: *M*, 102).

(ii) 2-*Chloro*-1,1,2-*trifluoroethylphosphonous dichloride.* This compound (0·40 g., 1·97 mmoles) was hydrolysed as above with 40% aqueous sodium hydroxide (10 ml., 100 mmoles) for 2 hr. at room temperature. Fractionation *in vacuo* yielded trifluoroethylene (0·12 g., 1·44 mmoles, 73%) (Found: *M*, 81. Calc. for C_2HF_3: *M*, 82) and 2-chloro-1,1,2-trifluoroethane (0·06 g., 0·51 mmoles, 26%) (Found: *M*, 118. Calc. for $C_2H_2ClF_3$: *M*, 118·5). In a separate experiment 2-chloro-1,1,2-trifluoroethane (0·11 g., 0·94 mmoles) was treated with 40% aqueous sodium hydroxide (10 ml., 100 mmoles) as above for 1 hr. at room temperature. The only volatile product was trifluoroethylene (0·07 g., 0·85 mmoles, 90%), identified by its molecular weight (Found: *M*, 81·5) and infrared spectrum.

(iii) 2,2-*Difluoroethylphosphonous dichloride.* This dichloride (0·24 g., 1·41 mmoles) was hydrolysed as above with 40% aqueous sodium hydroxide (10 ml., 100 mmoles), to yield acetylene (0·04 g., 1·42 mmoles, 100%) (Found: *M*, 27. Calc. for C_2H_2: *M*, 26). The basic hydrolysate contained fluoride ion.

1,1-Difluoroethane (0·20 g., 3·0 mmoles), when treated with 40% aqueous sodium hydroxide solution (10 ml., 100 mmoles) at room temperature for 2 hr., was recovered quantitatively in a control experiment. Vinyl fluoride was similarly inert under these conditions.

(iv) Hexafluoropropylphosphonous dichloride (0·71 g., 2·82 mmoles), a 2 : 1 mixture of $CF_3{\cdot}CHF{\cdot}CF_2{\cdot}PCl_2$ and $CF_3{\cdot}CF(PCl_2){\cdot}CHF_2$, was treated as above with 40% aqueous sodium hydroxide (10 ml., 100 mmoles) for 2 hr. at room temperature. Fractionation gave 1,1,1,2,3,3-hexafluoropropane (0·42 g., 2·76 mmoles, 98%) (Found: *M*, 151. Calc. for $C_3H_2F_6$: *M*, 152), identified by its infrared spectrum.

(v) *Tetrafluoroethylenediphosphonous dichloride.* This compound (0·57 g., 1·89 mmoles), hydrolysed as above with 40% aqueous sodium hydroxide (10 ml., 100 mmoles) for 2 hr. at room temperature, gave 1,1,2,2-tetrafluoroethane (0·19 g., 1·82 mmoles, 96%) (Found: *M*, 102. Calc. for $C_2H_2F_4$: *M*, 102).

Hydrolyses of Polyfluoroalkylphosphines.—The hydrolyses were carried out in a 300-ml. hydrolysis bulb as described above. Unless otherwise stated, an excess of 40% aqueous sodium hydroxide (10 ml., 100 mmole) was used, with a reaction time of 2 hr. at room temperature.

(i) 1,1,2,2-*Tetrafluoroethylphosphine.*—This compound (0·71 g., 5·29 mmoles) gave hydrogen (2·6 mmoles, 48%) (Found: *M*, 2·2), acetylene (0·01 g., 0·27 mmoles, 5%) (Found: *M*, 26·6. Calc. for C_2H_2: *M*, 26·0), and 1,2-difluoroethylene (0·30 g., 4·68 mmoles, 89%) (Found: *M*, 64. Calc. for $C_2H_2F_2$: *M*, 64).

In a control experiment sodium hypophosphite monohydrate (0·276 g., 2·60 mmoles), treated with 40% aqueous sodium hydroxide solution (10 ml., 100 mmoles) for 20 hr. at room temperature and then for 2 hr. at 50°, gave a quantitative yield of hydrogen (2·60 mmoles).

(ii) 2-*Chloro*-1,1,2-*trifluoroethylphosphine.* This compound (0·59 g., 3·88 mmole) gave hydrogen (1·84 mmoles, 48%), acetylene (0·01 g., 0·2 mmole, 5%) (Found: *M*, 27·4), and 1,2-difluoroethylene (0·18 g., 2·82 mmoles, 73%) (Found: *M*, 64).

(iii) *Hexafluoropropylphosphine.*—Hexafluoropropylphosphine (0·22 g., 1·20 mmoles), a 2 : 1 mixture of $CF_3{\cdot}CHF{\cdot}CF_2{\cdot}PH_2$ and $CF_3{\cdot}CF(PH_2){\cdot}CHF_2$, gave hydrogen (0·57 mmoles, 47%) and 1,3,3,3-tetrafluoropropene (0·13 g., 1·15 mmoles, 96%) (Found: *M*, 114. Calc. for $C_3H_2F_4$: *M*, 114), identified by its infrared spectrum. Gas-liquid chromatography of this compound on a 4-m. column (stationary phase, dinonyl phthalate) at room temperature showed only one peak.

(iv) *Bis*-1,1,2,2-*tetrafluoroethylphosphine.* This compound (0·51 g., 2·15 mmoles) gave 1,2-difluoroethylene and 1,1,2,2-tetrafluoroethane (4·24 mmoles, 99%) (Found: *M*, 84·7. Calc. for a 1 : 1 mixture of $C_2H_2F_2$ and $C_2H_2F_4$: *M*, 83·0) identified and analysed by their infrared spectra. No hydrogen was evolved.

(v) 2,2-*Difluoroethylphosphine.* This compound (0·23 g., 2·35 mmoles) was recovered quantitatively after treatment with 40% aqueous sodium hydroxide solution (10 ml., 100 mmoles) at room temperature for 2 hr.

Bis-1,1,2,2-*tetrafluoroethylphosphinous chloride.* This compound (0·46 g., 1·72 mmoles) gave 1,1,2,2-tetrafluoroethane (0·35 g., 3·35 mmoles, 97%) when treated with an excess of 40% aqueous sodium hydroxide at room temperature for 2 hr.

Preparation of Phosphonic Acids.—The phosphonic acids were prepared by hydrolysis of the corresponding phosphonous dichlorides with water at room temperature, followed by oxidation by boiling with unstabilised 80% hydrogen peroxide for 10 min. The resulting solutions were evaporated *in vacuo*, and the residual acids were dried in a vacuum-desiccator over phosphorus pentoxide.

(i) 1,1,2,2-Tetrafluoroethylphosphonous dichloride (0·32 g., 1·60 mmoles) was hydrolysed and oxidised, to yield white deliquescent needles of 1,1,2,2-*tetrafluoroethylphosphonic acid* (0·27 g., 1·50 mmoles, 94%) [Found: C, 13·2; H, 1·6%; Equiv., 89·5. $C_2H_3F_4O_3P$ requires C, 13·2; H, 1·7%; Equiv., 91·0], m. p. 50—51°. The equivalent weight and dissociation constants for this acid were determined by potentiometric titration against 0·5N-aqueous sodium hydroxide.

A *monoanilinium salt* was prepared by adding 1 ml. of aniline to a solution of 0·2 g. of the acid in 2 ml. of ethanol. The white precipitate was washed with ethanol and dried (Found: C, 34·9; H, 3·9; N, 5·1. $C_8H_{10}F_4NO_3P$ requires C, 34·9; H, 3·6; N, 5·1%); it had m. p. 225—228° (decomp.).

(ii) 2-Chloro-1,1,2-trifluoroethylphosphonous dichloride (0·47 g., 2·2 mmoles) was hydrolysed and oxidised as above, to yield deliquescent needles of 2-*chloro*-1,1,2-*trifluoroethylphosphonic acid* (0·42 g., 2·1 mmoles, 95%) (Found: C, 12·3; H, 1·6%; Equiv., 101. $C_2H_3ClF_3O_3P$ requires C, 12·1; H, 1·5%; Equiv., 99·5), m. p. 63—63·5°.

(iii) 2,2-Difluoroethylphosphonous dichloride (0·20 g., 1·20 mmoles) yielded the hygroscopic oily 2,2-*difluoroethylphosphonic acid* (0·163 g., 1·12 mmoles, 92%) (Found: C, 16·6; H, 3·5%; Equiv., 72·5. $C_2H_5F_2O_3P$ requires C, 16·4; H, 3·4%; Equiv., 73·0). The *monoanilinium salt* (Found: C, 40·1; H, 5·2; N, 6·0. $C_8H_{12}F_2NO_3P$ requires C, 40·2; H, 5·0; N, 5·9%), m. p. 224—226° (decomp.), was prepared as in (i).

(iv) Tetrafluoroethylenediphosphonous dichloride (0·40 g., 1·30 mmoles) similarly gave white crystals of *tetrafluoroethylenediphosphonic acid* (0·38 g., 1·20 mmoles, 92%) (Found: C, 9·0; H, 1·6%; Equiv., 66·0. $C_2H_4F_4O_6P_2$ requires C, 9·2; H, 1·5%; Equiv., 65·5), m. p. 89—92°. Potentiometric titration of the acid against aqueous sodium hydroxide gave a neutralisation curve with only 2 points of inflection, corresponding to dissociation constants of $3{\cdot}5 \times 10^{-2}$ and $3{\cdot}3 \times 10^{-6}$. The *dianilinium salt* (Found: C, 37·6; H, 4·1; N, 6·4. $C_{14}H_{18}F_4N_2O_6P_2$ requires C, 37·5; H, 4·0; N, 6·3%) had m. p. 235—238° (decomp.).

FACULTY OF TECHNOLOGY,
THE UNIVERSITY, MANCHESTER.

[*Received, May* 8*th*, 1963.]