1272. *Organophosphorus Chemistry. Part IV.*[1] *Phospha-alkenes as Intermediates in the Reaction of 1,1,2,2-Tetrafluoroethylphosphine with Dimethylamine or Aniline*

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1,1,2,2-Tetrafluoroethylphosphine reacts with dimethylamine to give 2,2-difluoroethyl-*NN*-dimethylphosphonamidous fluoride and 2,2-difluoroethyl-*NNN'N'*-tetramethylphosphonous diamide. Aniline affords the phospha-alkene 2,2-difluoroethylidene-*N*-phenylphosphinous amide, probably best regarded as 2,2-difluoroethyl-*N*-phenyliminophosphine, as a monomer in phenolic or methanolic solution, and possibly polymerised in absence of solvent. The formation of intermediate phospha-alkenes is postulated to explain these reactions.

PHOSPHA-ALKENES, $>\!C{=}P-$ or $>\!\overset{-}{C}-\overset{+}{P}-$, have been postulated [1,2] as intermediates in the reactions of primary or secondary phosphines containing the group $>\!CF{\cdot}PH-$ with aqueous base, with alcohols, or with ammonia. The reaction of a compound containing such a group with an aliphatic secondary amine and with an aromatic primary amine, now reported, gives support to the postulate of phospha-alkene formation.

Reaction of 1,1,2,2-tetrafluoroethylphosphine with an excess of dimethylamine in ether slowly gave dimethylamine hydrofluoride, 2,2-difluoroethyl-*NN*-dimethylphosphonamidous fluoride (I) (64% yield) and, as a minor product, 2,2-difluoroethyl-*NNN'N'*-tetramethylphosphonous diamide (II) (2% yield). The phosphonamidous fluoride reacted

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[1] Part III, H. Goldwhite, R. N. Haszeldine, and D. G. Rowsell, preceding Paper.

[2] G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J.*, 1964, 572; H. Goldwhite, R. N. Haszeldine, and D. G. Rowsell, *Chem. Comm.*, 1965, 83.

with anhydrous hydrogen chloride to give 2,2-difluoroethylphosphonous dichloride and difluoride, probably by the following route:

$$\underset{\text{(I)}}{CHF_2{\cdot}CH_2{\cdot}PF{\cdot}NMe_2} \xrightarrow{HCl} Me_2\overset{+}{N}H_2Cl^- + CHF_2{\cdot}CH_2{\cdot}PFCl$$

$$2CHF_2{\cdot}CH_2{\cdot}PFCl \xrightarrow{Me_2\overset{+}{N}H_2Cl^-} CHF_2{\cdot}CH_2{\cdot}PCl_2 + CHF_2{\cdot}CH_2{\cdot}PF_2$$

2,2-Difluoroethylphosphonous dichloride and difluoride, and thence the phosphonamidous fluoride (I) and the diamide (II), were identified by comparison with authentic samples prepared as follows:

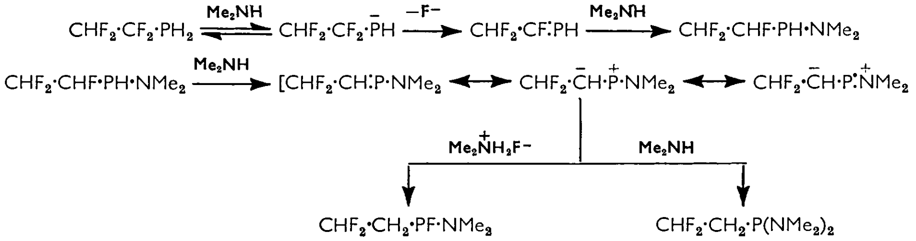
$$\begin{tikzcd}
CH_2{:}CF_2 \arrow[r, "PH_3"] & CHF_2{\cdot}CH_2{\cdot}PH_2 \arrow[r, "COCl_2"] & CHF_2{\cdot}CH_2{\cdot}PCl_2 \arrow[r, "SbF_3"] \arrow[d, "Me_2NH"] & CHF_2{\cdot}CH_2{\cdot}PF_2 \arrow[d, "Me_2NH"] \\
 & & \text{(II)} & \text{(I)} \arrow[l, "Me_2NH"']
\end{tikzcd}$$

Treatment of the diamide (II) with an excess of dry hydrogen chloride also gave 2,2-difluoroethylphosphonous dichloride.

The infrared (i.r.) spectrum of the phosphonamidous fluoride (I) showed bands at 10·1 (P–NMe$_2$) and 12·0μ (P–F). The ^{19}F n.m.r. spectrum had bands at 110·2 (multiplet) and 119·5 p.p.m. (doublet, $J = 886$ c./sec.) from CFCl$_3$, with area ratio of 2 : 1, respectively; the doublet confirms the presence of a P–F bond. The mass spectrum showed peaks at *m/e* 159 (weak parent ion), 113, 69, and 42·1 (metastable) corresponding to the process:

$$[CHF_2{\cdot}CH_2{\cdot}PF{\cdot}NMe_2]^+ \longrightarrow [F_2P{\cdot}NMe_2]^+ \longrightarrow [PF_2]^+$$

The above evidence shows clearly that both α-fluorines have been lost from the original tetrafluoroethyl group in the phosphine, and a mechanism involving phospha-alkene intermediates accounts for this:



$$CHF_2{\cdot}CF_2{\cdot}PH_2 \overset{Me_2NH}{\rightleftharpoons} CHF_2{\cdot}CF_2{\cdot}\overset{-}{P}H \xrightarrow{-F^-} CHF_2{\cdot}CF{:}PH \xrightarrow{Me_2NH} CHF_2{\cdot}CHF{\cdot}PH{\cdot}NMe_2$$

$$CHF_2{\cdot}CHF{\cdot}PH{\cdot}NMe_2 \xrightarrow{Me_2NH} [CHF_2{\cdot}CH{:}P{\cdot}NMe_2 \longleftrightarrow CHF_2{\cdot}\overset{-}{C}H{\cdot}\overset{+}{P}{\cdot}NMe_2 \longleftrightarrow CHF_2{\cdot}\overset{-}{C}H{\cdot}P{:}\overset{+}{N}Me_2$$

$$\xrightarrow{Me_2\overset{+}{N}H_2F^-} CHF_2{\cdot}CH_2{\cdot}PF{\cdot}NMe_2 \qquad \xrightarrow{Me_2NH} CHF_2{\cdot}CH_2{\cdot}P(NMe_2)_2$$

The greater selectivity of the second phospha-alkene shown by its preferred addition reaction with amine hydrofluoride rather than with amine may be attributed to the additional stabilisation obtained by interaction with the lone pair on nitrogen, which is not possible for the first phospha-alkene. Control experiments showed that the phosphonamidous fluoride is not formed from the diamide by reaction with dimethylamine hydrofluoride under the conditions of the tetrafluoroethylphosphine–dimethylamine reaction.

Aniline reacts slowly with 1,1,2,2-tetrafluoroethylphosphine in ether to give aniline hydrofluoride and a solid, m. p. 160°. Elemental analyses on the solid reveal an empirical formula $C_8H_8F_2PN$ corresponding to $CHF_2{\cdot}[CH_2P]{\cdot}NPh$. The solid dissolves in phenol and in methanol in low concentration, and determination of molecular weights in these solvents, shows that in solution the solid exists as a monomer, implying that the phospha-alkene 2,2-difluoroethylidene-*N*-phenylphosphinous amide (III) or more probably its tautomer 2,2-difluoroethyl-*N*-phenyliminophosphine (IV) is stable in solution. Attempts to isolate the monomer from the solution were unsuccessful and only the solid, m. p. 160°, was obtained. The low solubility of the solid precluded n.m.r. measurements. It is not yet known whether the solid, m. p. 160°, is a monomer (III) or (IV), or a polymer derived from it.

The reaction of 1,1,2,2-tetrafluoroethylphosphine with aniline probably proceeds by a phospha-alkene mechanism of the type suggested for the reaction with dimethylamine:

$$\mathrm{CHF_2{\cdot}CF_2{\cdot}PH_2 \xrightarrow{PhNH_2} CHF_2{\cdot}CF{:}PH \xrightarrow{PhNH_2} CHF_2{\cdot}CHF{\cdot}PH{\cdot}NHPh \xrightarrow{PhNH_2} CHF_2{\cdot}CH{:}P{\cdot}NHPh}$$

$$[\mathrm{CHF_2{\cdot}CH{:}P{\cdot}NHPh} \longleftrightarrow \underset{\text{(III)}}{\mathrm{CHF_2{\cdot}\overset{-}{C}H{\cdot}\overset{+}{P}{\cdot}NHPh}} \longleftrightarrow \mathrm{CHF_2{\cdot}\overset{-}{C}H{\cdot}P{:}\overset{+}{N}HPh}] \rightleftharpoons$$

$$[\mathrm{CHF_2{\cdot}CH_2{\cdot}P{:}NPh} \longleftrightarrow \underset{\text{(IV)}}{\mathrm{CHF_2{\cdot}CH_2{\cdot}\overset{+}{P}{\cdot}\overset{-}{N}Ph}}]$$

$$\text{(IV)} \longrightarrow [\mathrm{CHF_2{\cdot}CH_2{\cdot}P{\cdot}NPh}]_n$$

The very low solubility of the solid, m. p. 160°, also hinders most attempts at investigation of chemical properties. However, the solid reacts rapidly with aqueous hydrochloric acid, and after removal of aniline hydrochloride from the acid hydrolysate by use of a cation-exchange resin, and oxidation with hydrogen peroxide, the known 2,2-difluoroethylphosphonic acid $\mathrm{CHF_2{\cdot}CH_2{\cdot}PO(OH)_2}$ was obtained as the mono-anilinium salt. This shows clearly that the product of the reaction of 1,1,2,2-tetrafluoroethylphosphine with aniline contains the $\mathrm{CHF_2{\cdot}CH_2{\cdot}P}$ group.

The liberation of acetylene on aqueous alkaline hydrolysis of the solid of m. p. 160°, or of the diamide (V), and formation of aniline or dimethylamine, also provides evidence for the $\mathrm{CHF_2{\cdot}CH_2{\cdot}P}$ group; 2,2-difluoroethylphosphonous acid is known to liberate acetylene when similarly hydrolysed.[3]

$$[\mathrm{CHF_2{\cdot}CH_2{\cdot}P{\cdot}NPh}]_n \text{ or } \underset{\text{(V)}}{\mathrm{CHF_2{\cdot}CH_2{\cdot}P(NMe_2)_2}} \xrightarrow{\mathrm{OH^-}} \mathrm{CHF_2{\cdot}CH_2{\cdot}P(OH)_2}$$

$$\mathrm{CHF_2{\cdot}CH_2{\cdot}P(OH)_2 \xrightarrow{OH^-} CHF{:}CH{\cdot}P(OH)_2 \xrightarrow{OH^-} H_3PO_3 + CHF{:}CH^- \longrightarrow F^- + C_2H_2}$$

EXPERIMENTAL

Volatile products were manipulated in a conventional vacuum system.

Preparation of 2,2-*Difluoroethylphosphonous Difluoride*.—1,1-Difluoroethylene (57·6 g., 0·93 mole) and phosphine (30·6 g., 0·90 mole), heated at 230—240° in a 1-l. autoclave for 5 days, gave 2,2-difluoroethylphosphine (25·0 g., 0·36 mole, 40%) identical with the compound prepared [1] by the photochemical route.

2,2-Difluoroethylphosphine (5·2 g., 53 mmoles) and phosgene (11·6 g., 117 mmoles), allowed to warm up from −78° to room temperature in a 300-ml. autoclave and then kept for 16 hr., gave hydrogen chloride (4·2 g., 115 mmoles), carbon monoxide, and 2,2-difluoroethylphosphonous dichloride (7·2 g., 43 mmoles, 81%), identical with the sample prepared [1] by the action of chlorine on 2,2-difluoroethylphosphine.

Powdered antimony trifluoride (6·0 g.) and 2,2-difluoroethylphosphonous dichloride (4·5 g., 27 mmoles), kept at 20° for 1 hr. in a 300-ml. tube, gave 2,2-*difluoroethylphosphonous difluoride* (2·1 g., 16 mmoles, 59%) (Found: C, 17·9; H, 2·2%; *M*, 135. $\mathrm{C_2H_3F_4P}$ requires C, 17·9; H, 2·2%; *M*, 134), with bands in the i.r. region at 3·3m, 7·1w, 7·3s, 8·0w, 8·25w, 8·4s, 9·0w, 9·4vs, 9·8w, 10·2s, 12·0w, 12·4vs, 13·2s μ.

Reaction of 1,1,2,2-*Tetrafluoroethylphosphine with Dimethylamine*.—Dimethylamine (15·0 g., 0·333 mole) in dry ether (150 ml.) reacted slowly with 1,1,2,2-tetrafluoroethylphosphine [3] (3·6 g., 27 mmoles) in a 350-ml. tube, and crystals of dimethylamine hydrofluoride slowly precipitated. After 2 days at 20° the reaction mixture was filtered in an atmosphere of dry nitrogen, and the filtrate fractionated *in vacuo* to give 2,2-*difluoroethyl*-NN-*dimethylphosphonamidous fluoride* (2·7 g., 17 mmoles, 64%) (Found: C, 30·5; H, 5·4; N, 9·1%; *M*, 161. $\mathrm{C_4H_9F_3NP}$ requires C, 30·2; H, 5·6; N, 8·8%; *M*, 159) as a colourless, relatively volatile, liquid.

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[3] G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J.*, 1963, 1083.

Its i.r. spectrum showed bands at 3·3vw, 3·4w, 7·1vw, 7·25vw, 7·3w, 7·8m, 8·2m, 8·4w, 8·95w, 9·4s, 9·85w, 10·1s, 12·0s, 13·6 w μ.

A small quantity (0·10 g., 2%) of a less volatile compound was identified as 2,2-difluoroethyl-*NNN'N'*-tetramethylphosphonous diamide, by comparison of its i.r. spectrum with that of an authentic sample, and by reaction with an excess of anhydrous hydrogen chloride at 20° to give 2,2-difluoroethylphosphonous dichloride (91% yield) and dimethylamine hydrochloride (96% yield).

Reaction of 2,2-*Difluoroethyl*-NN-*dimethylphosphonamidous Fluoride with Hydrogen Chloride.*—The phosphonamidous fluoride (1·4 g., 8·8 mmoles) and hydrogen chloride (2·2 g., 59 mmoles), kept in a 350-ml. tube at room temperature for 3 hr., gave 2,2-difluoroethylphosphonous dichloride (0·68 g., 4·1 mmoles, 47%) (Found: *M*, 165. Calc. for $C_2H_3Cl_2F_2P$: *M*, 167) and 2,2-difluoroethylphosphonous difluoride (0·43 g., 3·2 mmoles, 37%) (Found: *M*, 136. Calc. for $C_2H_3F_4P$: *M*, 134), both identified spectroscopically.

Reaction of 2,2-*Difluoroethylphosphonous Dichloride with Dimethylamine.*—Dimethylamine (7·2 g., 160 mmoles) and 2,2-difluoroethylphosphonous dichloride (3·1 g., 19 mmoles), kept in a 60-ml. tube for 2 hr. at 20° gave 2,2-*difluoroethyl*-NNN'N'-*tetramethylphosphonous diamide* (2·50 g., 14 mmoles, 75%) (Found: C, 38·9; H, 7·8; N, 15·0. $C_6H_{15}F_2N_2P$ requires C, 39·2; H, 8·1; N, 15·2%), as a colourless viscous oil.

Reaction of 2,2-*Difluoroethylphosphonous Difluoride with Dimethylamine.*—Dimethylamine (1·4 g., 32 mmoles) and 2,2-difluoroethylphosphonous difluoride (1·05 g., 8·0 mmoles), kept in a 60-ml. tube for 2 days at 20° gave 2,2-difluoroethyl-*NN*-dimethylphosphonamidous fluoride (0·48 g., 3·0 mmoles, 37%) and 2,2-difluoroethyl-*NNN'N'*-tetramethylphosphonous diamide (0·85 g., 4·6 mmoles, 58%), both identical (n.m.r. and i.r.) with the corresponding products from the 1,1,2,2-tetrafluoroethylphosphine–dimethylamine reaction.

Reaction of 2,2-*Difluoroethyl*-NN-*dimethylphosphonamidous Fluoride with Dimethylamine.*—Dimethylamine (0·76 g., 17 mmoles) and 2,2-difluoroethyl-*NN*-dimethylphosphonamidous fluoride (1·35 g., 8·5 mmoles), kept in a 20-ml. tube for 7 days at 20° gave 2,2-difluoroethyl-*NNN'N'*-tetramethylphosphonous diamide (1·46 g., 8·0 mmoles, 94%), identified spectroscopically (n.m.r.).

Reaction of 1,1,2,2-*Tetrafluoroethylphosphine with Aniline.*—Aniline (19·5 g., 200 mmoles) and 1,1,2,2-tetrafluoroethylphosphine (7·0, 50 mmoles) in dry ether (200 ml.) contained in a 350-ml. tube were heated at 100° for 6 days. A yellow solid was precipitated, which on sublimation *in vacuo* gave aniline hydrofluoride, $C_6H_5NH_2,4HF$, m. p. 192° (*subl.*), and 2,2-*difluoroethyl*-N-*phenyliminophosphine* (8·0 g., 43 mmoles, 86%), m. p. 160° [Found: C, 52·0; H, 4·3; N, 7·6%; *M* (in phenol), 200; *M* (in methanol), 185. $C_8H_8F_2NP$ requires C, 52·0; H, 4·3; N, 7·6%; *M*, 187]. Addition of anhydrous ether to the phenolic or methanolic solution precipitated the solid, m. p. 160°. The i.r. spectrum (Nujol) of the solid showed only diffuse bands at 3—15 μ.

Reaction of 2,2-*Difluoroethyl*-N-*phenyliminophosphine with Aqueous Hydrochloric Acid.*—The iminophosphine (0·50 g., 2·7 mmoles) was warmed in 5N-hydrochloric acid (30 ml.) for 30 min. The resultant solution was freeze-dried, and the residue was dissolved in water and passed down a column of a sulphonated polystyrene cation-exchange resin (H^+ form). The eluate was warmed with 30% hydrogen peroxide (10 ml.) for 30 min. and freeze-dried. The resultant viscous oil (0·2 g.) was dissolved in ethanol (2 ml.) and aniline (1 ml.) added to precipitate the monoanilinium salt of 2,2-difluoroethylphosphonic acid (0·30 g., 1·2 mmoles, 45%) (Found: C, 39·8; H, 5·3; N, 5·7. Calc. for $C_8H_{12}F_2NO_3P$: C, 40·2; H, 5·0; N, 5·9%), m. p. 224° (decomp.) [lit.,[2] 225° (decomp.)].

Reaction of 2,2-*Difluoroethyl*-NNN'N'-*tetramethylphosphonous Diamide with Aqueous Sodium Hydroxide.*—The diamide (0·70 g., 4·0 mmoles) kept with aqueous 40% sodium hydroxide (20 ml.) in an evacuated bulb for 24 hr. at room temperature gave acetylene (0·052 g., 2·0 mmoles, 50%) and dimethylamine (0·158 g., 3·5 mmoles, 45%), identified by i.r. spectroscopy.

Reaction of 2,2-*Difluoroethyl*-N-*phenyliminophosphine with Aqueous Sodium Hydroxide.*—The iminophosphine (2·0 g., 10 mmoles), hydrolysed with 40% aqueous sodium hydroxide (20 ml.) gave acetylene (0·156 g., 6·0 mmoles, 60%) and aniline (0·60 g., 6·5 mmoles, 65%), identified as acetanilide.

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