1271. *Organophosphorus Chemistry. Part III.*[1] *The Reactions of Phospha-alkenes with Nucleophiles and as Intermediates in Polymer Synthesis*[2]

By H. Goldwhite, R. N. Haszeldine, and D. G. Rowsell

Elimination of hydrogen fluoride from the group $>$CF·PH– is believed to give a phospha-alkene, $>$C=P–, as an intermediate which rapidly reacts by addition with alcohols or ammonia. Phospha-alkenes are postulated as intermediates in polymer formation from primary αα-dihalogenophosphines and ammonia.

The products of the aqueous alkaline hydrolysis of polyfluoroalkylphosphines such as $CHF_2{\cdot}CF_2{\cdot}PH_2$ and $(CHF_2{\cdot}CF_2)_2PH$ led to the postulation of phospha-alkenes, $>$C=P– or $>\overset{-}{C}-\overset{+}{P}-$, as intermediates.[1] The reactions of halogenoalkylphosphines with other nucleophiles such as alkoxides or ammonia, now reported, can be interpreted on a similar basis.

Secondary Phosphines.—The reaction of methanolic sodium methoxide with bistrifluoromethylphosphine gives methyl difluoromethyltrifluoromethylphosphinite in 35% yield:

$$(CF_3)_2PH \overset{MeO^-,\ <0^\circ}{\rightleftharpoons} (CF_3)_2P^- \xrightarrow{-F^-} CF_3{\cdot}P{:}CF_2 \xrightarrow{MeOH} CF_3{\cdot}P(OMe){\cdot}CHF_2$$

The proton magnetic resonance (p.m.r.) spectrum of the last compound shows a doublet (τ 6·08, $J_{CH_3{\cdot}P}$ = 13·8 c./sec.) and a triplet of doublets (τ 3·72, J_{HF} = 50·4 and $J_{H{\cdot}P}$ = 7·4 c./sec.) with an area ratio of 3 : 1, respectively, confirming the presence of the group $CHF_2{\cdot}P{\cdot}OCH_3$ in the compound. At higher temperature (20—40°) the difluoromethyltrifluoromethylphosphinite reacts further, but relatively slowly:

$$CF_3{\cdot}P(OMe){\cdot}CHF_2 \xrightarrow{MeO^-,\ MeOH} CHF_3\ (100\%) + CHF_2{\cdot}P(OMe)_2$$

Ethanolic ethoxide reacts similarly with bistrifluoromethylphosphine to give ethyl difluoromethyltrifluoromethylphosphinite.

Ammonia rapidly converts bistrifluoromethylphosphine into difluoromethyltrifluoromethylphosphinamide (64% yield):

$$(CF_3)_2PH + NH_3 \longrightarrow NH_4F + CF_3{\cdot}P{:}CF_2 \xrightarrow{NH_3} CF_3{\cdot}P(NH_2){\cdot}CHF_2$$

The C–H stretching frequency at 2960 cm.$^{-1}$, the absence of a P–H stretching frequency, and the ready reaction of the phosphinamide with dry hydrogen chloride, which shows the presence of a P–N bond,

$$CF_3{\cdot}P(NH_2){\cdot}CHF_2 + 2HCl \longrightarrow CF_3{\cdot}PCl{\cdot}CHF_2\ (78\%) + NH_4Cl$$

eliminate the possibility of the alternative formula $CF_3{\cdot}PH{\cdot}CF_2{\cdot}NH_2$. A compound with the last formula would be expected to lose hydrogen fluoride from the $-CF_2{\cdot}NH_2$ group

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[1] Part II, G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J.*, 1964, 572.

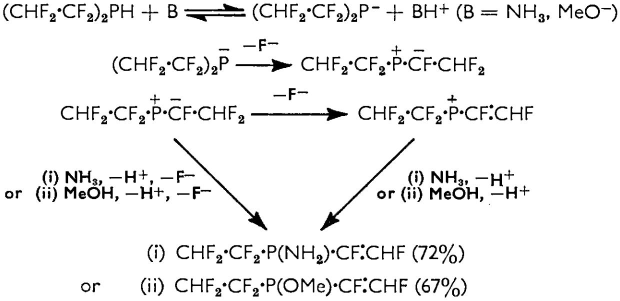
[2] H. Goldwhite, R. N. Haszeldine, and D. G. Rowsell, *Chem. Comm.*, 1965, 83.

very rapidly in a polar basic medium. The hydrolysis of the phosphinamide or of the phosphinous chloride:

$$CF_3{\cdot}PX{\cdot}CHF_2 \xrightarrow{H_2O,\ OH^-} CHF_3\ (100\%;\ X = NH_2 \text{ or Cl})$$

shows the presence of one trifluoromethyl group.

The reactions of the secondary phosphine, bis-(1,1,2,2-tetrafluoroethyl)phosphine, with ammonia or with methanolic methoxide are similar to those of bistrifluoromethylphosphine, except that one of the fluoroalkyl groups is dehydrofluorinated, as shown by a strong C⁚C stretching absorption at *ca.* 1670 cm.$^{-1}$ in the products.



$$(CHF_2{\cdot}CF_2)_2PH + B \rightleftharpoons (CHF_2{\cdot}CF_2)_2P^- + BH^+\ (B = NH_3,\ MeO^-)$$

$$(CHF_2{\cdot}CF_2)_2\bar{P} \xrightarrow{-F^-} CHF_2{\cdot}CF_2{\cdot}\overset{+}{P}{\cdot}\overset{-}{C}F{\cdot}CHF_2$$

$$CHF_2{\cdot}CF_2{\cdot}\overset{+}{P}{\cdot}\overset{-}{C}F{\cdot}CHF_2 \xrightarrow{-F^-} CHF_2{\cdot}CF_2{\cdot}\overset{+}{P}{\cdot}CF{:}CHF$$

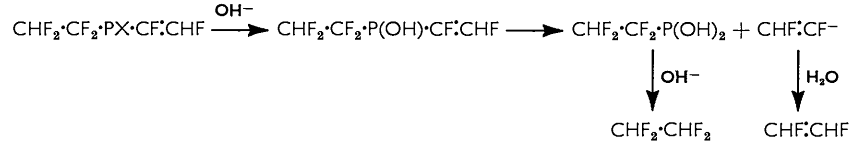
(i) NH$_3$, –H$^+$, –F$^-$ or (ii) MeOH, –H$^+$, –F$^-$; (i) NH$_3$, –H$^+$ or (ii) MeOH, –H$^+$

(i) $CHF_2{\cdot}CF_2{\cdot}P(NH_2){\cdot}CF{:}CHF$ (72%)

or (ii) $CHF_2{\cdot}CF_2{\cdot}P(OMe){\cdot}CF{:}CHF$ (67%)

Formation of methyl 1,1,2,2-tetrafluoroethyl-1,2-difluorovinylphosphinite and of 1,1,2,2-tetrafluoroethyl-1,2-difluorovinylphosphinamide *via* loss of fluoride from the carbanion as above seems more likely than the formation of the compounds $CHF_2{\cdot}CF_2{\cdot}PX{\cdot}CHF{\cdot}CHF_2$ ($X = NH_2$ or OMe) followed by dehydrofluorination of the trifluoroethyl group under the mild conditions used (*e.g.*, ammonia, 1 hr., 20°).

The reaction of the compounds $CHF_2{\cdot}CF_2{\cdot}PX{\cdot}CF{:}CHF$ ($X = NH_2$ or OMe) with aqueous sodium hydroxide to give an equimolar mixture of 1,2-difluoroethylene and 1,1,2,2-tetrafluoroethane,

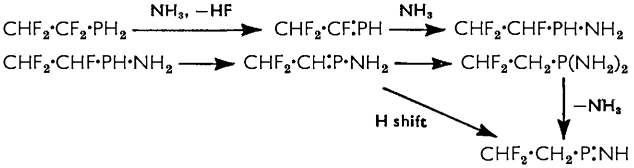


$$CHF_2{\cdot}CF_2{\cdot}PX{\cdot}CF{:}CHF \xrightarrow{OH^-} CHF_2{\cdot}CF_2{\cdot}P(OH){\cdot}CF{:}CHF \longrightarrow CHF_2{\cdot}CF_2{\cdot}P(OH)_2 + CHF{:}CF^-$$

$$CHF_2{\cdot}CF_2{\cdot}P(OH)_2 \xrightarrow{OH^-} CHF_2{\cdot}CHF_2 \qquad CHF{:}CF^- \xrightarrow{H_2O} CHF{:}CHF$$

is fully consistent with the structures suggested and with the mechanism advanced for the aqueous alkaline hydrolysis of bis-(1,1,2,2-tetrafluoroethyl)phosphine[3] to give 1,2-difluoroethylene (50%) and 1,1,2,2-tetrafluoroethane (50%).[1]

Primary Phosphines.—The reaction of primary αα-dihalogenophosphines with ammonia or amines leads to novel polymers considered to arise *via* phospha-alkene formation. Thus 1,1,2,2-tetrafluoroethylphosphine reacts rapidly with liquid ammonia at –78° to give a solid polymer containing a P–N network and of empirical formula $C_6H_9F_6N_2P_3$; the polymer has good thermal stability (400°) and is unattacked by aqueous alkali or by non-oxidising acids. The empirical formula suggests a polymer $[(CHF_2{\cdot}CH_2{\cdot}P)_3N_2]_n$ containing linear or cyclic units or both, in which both fluorines α to phosphorus have been replaced by hydrogen. The following scheme, in which it will be noted that the phospha-alkene becomes converted into a –P⁚N– intermediate, is suggested:



$$CHF_2{\cdot}CF_2{\cdot}PH_2 \xrightarrow{NH_3,\ -HF} CHF_2{\cdot}CF{:}PH \xrightarrow{NH_3} CHF_2{\cdot}CHF{\cdot}PH{\cdot}NH_2$$

$$CHF_2{\cdot}CHF{\cdot}PH{\cdot}NH_2 \longrightarrow CHF_2{\cdot}CH{:}P{\cdot}NH_2 \longrightarrow CHF_2{\cdot}CH_2{\cdot}P(NH_2)_2$$

$$CHF_2{\cdot}CH{:}P{\cdot}NH_2 \xrightarrow{\text{H shift}} CHF_2{\cdot}CH_2{\cdot}P{:}NH \qquad CHF_2{\cdot}CH_2{\cdot}P(NH_2)_2 \xrightarrow{-NH_3} CHF_2{\cdot}CH_2{\cdot}P{:}NH$$

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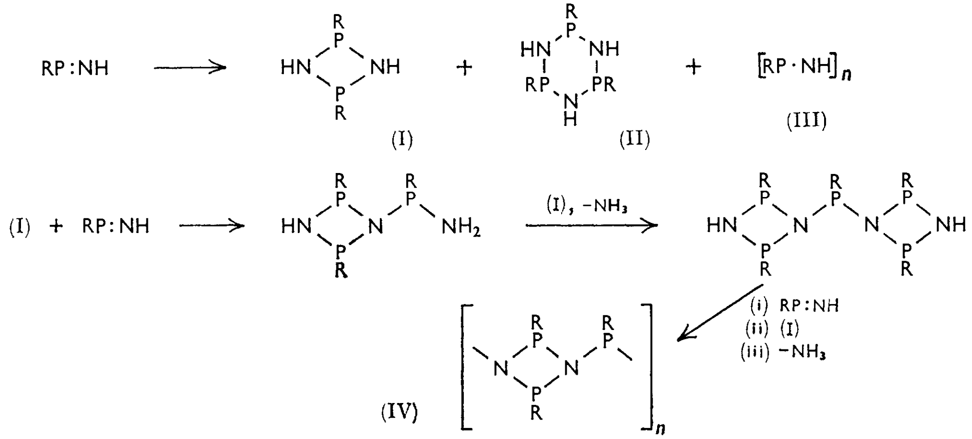
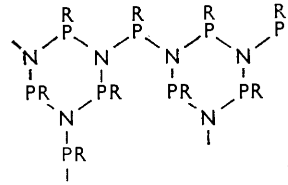
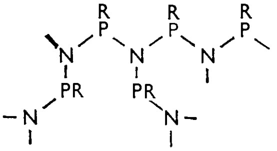
[3] G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J.*, 1963, 1083.

then, where R = $CHF_2{\cdot}CH_2$,

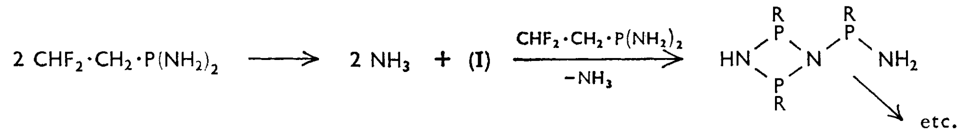


Reaction of RP:NH with each of the NH groups in (II) or (III) affords lattice or cross-linked structures (V) or (VI):


(V)


(VI)

Intermolecular loss of ammonia from the intermediate diamide $CHF_2{\cdot}CH_2{\cdot}P(NH_2)_2$ could yield similar units without the formation of $CHF_2{\cdot}CH_2{\cdot}P{:}NH$ as an intermediate, *e.g.*,



The reactions of primary αα-dihalogenophosphines with primary and secondary amines[4] provide strong support for the above general mechanisms for polymerisation *via* phosphaalkenes.

EXPERIMENTAL

Volatile products were manipulated in a conventional vacuum system.

Bistrifluoromethylphosphine.—Pressure hydrogenation enabled this compound[5] to be prepared on a relatively large scale and in improved yield. Raney nickel (30 g.) was added as a slurry in ethanol to a 1 l.-autoclave, and the ethanol was removed by pumping at 20° for 8 hr. Bistrifluoromethylphosphinous iodide[5] (55·2 g., 0·187 mole) was then condensed in, and after attaining room temperature the autoclave was pressurised with 20 atm. of hydrogen, then heated in a rocking furnace for 48 hr. at 145—150°. The volatile products were distilled *in vacuo* and then at atmospheric pressure to give spectroscopically pure bistrifluoromethylphosphine (22·1 g., 0·130 mole; 70%) (Found: C, 14·3; H, 0·8%; *M*, 171. Calc. for C_2HF_6P: C, 14·1; H, 0·6%; *M*, 170), b. p. 0·5—1·0°.

Reactions of Bistrifluoromethylphosphine.—(a) *With methanolic methoxide.* A mixture of sodium methoxide (1·03 g., 19·0 mmoles) in dry methanol (6 ml.) and bistrifluoromethylphosphine (4·10 g., 24·1 mmoles) in a 350 ml. tube, allowed to warm up from −196° to 0°, began to react at well below −20° and gave sodium fluoride, fluoroform (0·05 g., 0·7 mmole, 3%), bistrifluoromethylphosphine (0·92 g., 5·41 mmoles, 22%), and a fraction shown by infrared spectroscopy

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[4] M. Green, R. N. Haszeldine, B. R. Iles, and D. G. Rowsell, Part IV, and subsequent Papers.

[5] F. W. Bennett, H. J. Emeleus, and R. N. Haszeldine, *J.*, 1953, 1565; 1954, 3598, 3896.

to contain methanol and a compound containing C–F bonds. The last fraction was condensed into a 40 ml. tube and shaken with water (20 ml.) for 15 min. The immiscible liquid was removed by pumping, again shaken with water (10 ml.), then dried (P_4O_{10}; 14 hr.), and distilled *in vacuo* to give *methyl difluoromethyltrifluoromethylphosphinite* (1·20 g., 6·60 mmoles; 35%) (Found: C, 19·8; H, 2·0%; *M*, 183. $C_3H_4OF_5P$ requires C, 19·8; H, 2·2%; *M*, 182), b. p. 63° (isoteniscope).

Methyl difluoromethyltrifluoromethylphosphinite (0·20 g., 1·1 mmole), heated with water (4 ml.) in a sealed tube at 70° for 12 hr., gave fluoroform (0·085 g., 1·2 mmole; 100%) (Found: *M*, 69·5. Calc. for CHF_3: *M*, 70).

(*b*) *With sodium methoxide.* Sodium methoxide (1·62 g., 30·0 mmoles) in dry methanol (10 ml.) was added to a 350 ml. tube, and the methanol was removed by pumping (note: the residue is probably CH_3ONa,CH_3OH); bistrifluoromethylphosphine (7·00 g., 41·2 mmoles) was then condensed in. A vigorous exothermic reaction occurred as the tube warmed from −196° to 0°. Fractionation gave (i) fluoroform (0·84 g., 12·0 mmoles; 29%) (Found: *M*, 69·6. CHF_3 requires *M*, 70), (ii) unchanged bistrifluoromethylphosphine (3·40 g., 20·0 mmoles, 48%), (iii) a mixture of methanol and methyl difluoromethyltrifluoromethylphosphinite, which when treated with water, dried, and distilled as described above gave methyl difluoromethyltrifluoromethylphosphinite (0·90 g., 5·00 mmoles; 23%), and (iv) a liquid of higher b. p. which was purified by fractional condensation to give *dimethyl difluoromethylphosphonite* (0·70 g., 4·86 mmoles; 23%) (Found: C, 24·8; H, 4·7%; *M*, 144. $C_3H_7O_2F_2P$ requires C, 25·0; H, 4·9%; *M*, 144) b. p. 107° (isoteniscope).

(c) *With ethanolic ethoxide.* Sodium ethoxide (0·083 g., 1·22 mmoles) in ethanol (2 ml.) and bistrifluoromethylphosphine (0·292 g., 1·72 mmoles) in a 40-ml. tube allowed to warm from −196° to room temperature gave sodium fluoride, bistrifluoromethylphosphine (0·085 g., 0·50 mmole, 29%) and a fraction which was treated with water and dried as described in (a) to give *ethyl difluoromethyltrifluoromethylphosphinite* (0·074 g., 0·38 mmole; 31%) (Found: C, 24·3; H, 3·2%; *M*, 198. $C_4H_6OF_5P$ requires C, 24·5; H, 3·1%; *M*, 196), b. p. 78° (isoteniscope).

(d) *With ammonia.* Approximately 15 mmoles of ammonia and 4 mmoles of bistrifluoromethylphosphine were condensed into each of nine 40-ml. tubes. The total amounts were ammonia (2·24 g., 132 mmoles) and bistrifluoromethylphosphine (6·09 g., 36 mmoles). White solid was deposited in each tube soon after it had been removed from the liquid nitrogen, and reaction was complete when the tubes reached room temperature. The combined products were fractionated to give ammonia (0·80 g., 47 mmoles) and *difluoromethyltrifluoromethylphosphinamide* (3·80 g., 23 mmoles; 64%) (Found: C, 14·4; H, 1·7; F, 56·7; N, 8·5%; *M*, 168. $C_2H_3F_5NP$ requires C, 14·4; H, 1·8; F, 56·9; N, 8·4%; *M*, 167), b. p. 92—93°.

The amide (0·105 g., 0·60 mmole) and water (3 ml.) heated in a sealed tube at 70° for 14 hr. gave fluoroform (0·045 g., 0·60 mmole; 100%) (Found: *M*, 69).

Difluoromethyltrifluoromethylphosphinamide (0·154 g., 0·92 mmole) and an excess of hydrogen chloride (0·150 g., 4·10 mmoles) in a 350-ml. tube gave a white solid as soon as the tube warmed up to room temperature. After a further 15 min., fractionation gave hydrogen chloride (0·077 g., 2·11 mmoles) and *difluoromethyltrifluoromethylphosphinous chloride* (0·135 g., 0·72 mmole, 78%) (Found: C, 12·8; H, 0·3; Cl, 19·3%; *M*, 188. C_2HClF_5P requires C, 12·9; H, 0·5; Cl, 19·0%; *M*, 187), b. p. 37° (isoteniscope). The phosphinous chloride (0·155 g., 0·83 mmole) and 10% aqueous sodium hydroxide (10 ml.), kept for 14 hr. at 20° in a sealed tube, gave fluoroform (0·059 g., 0·83 mmole, 100%) (Found: *M*, 69·5).

Reactions of Bis-(1,1,2,2-*tetrafluoroethyl*)*phosphine*.—(a) *With sodium methoxide.* Sodium methoxide (0·39 g., 7·20 mmoles) in methanol (5 ml.) was added to a 40-ml. tube and the methanol was removed by pumping. Bis-(1,1,2,2-tetrafluoroethyl)phosphine [3] (0·95 g., 4·08 mmole) was condensed in and after 30 min. at room temperature the volatile products were fractionated *in vacuo* to give methanol, bis-(1,1,2,2-tetrafluoroethyl)phosphine, and *methyl* 1,2-*difluorovinyl*-1,1,2,2-*tetrafluoroethylphosphinite* (0·618 g., 2·73 mmoles, 67%) (Found: C, 26·2; H, 2·1. $C_5H_5OF_6P$ requires C, 26·6; H, 2·2%), ν(C⁚C) 1667 cm.$^{-1}$

The phosphinite (0·30 g., 1·33 mmoles) was condensed into a hydrolysis bulb, 40% aqueous sodium hydroxide (20 ml.) was run in, and the bulb was shaken for 15 min. to give a mixture (0·186 g., 2·25 mmoles, 84%; *M*, 82·3) shown by infrared spectroscopy to contain only 1,1,2,2-tetrafluoroethane and 1,2-difluoroethylene, the yields of which, calculated from the molecular weight of the mixture were 1·11 mmoles (83%) and 1·14 mmoles (86%), respectively.

(b) *With ammonia.* Bis-(1,1,2,2-tetrafluoroethyl)phosphine (0·957 g., 4·08 mmoles) and ammonia (0·46 g., 26·9 mmoles) were condensed into a 250-ml. tube which was warmed to room temperature then kept for 3 hr. Distillation of the volatile products gave ammonia (0·27 g., 16·0 mmoles), and 1,2-*difluorovinyl*-1,1,2,2-*tetrafluoroethylphosphinamide* (0·610 g., 2·92 mmoles; 72%) (Found: C, 22·6; H, 1·7; N, 6·5%. $C_4H_4F_6NP$ requires C, 22·8; H, 1·9; N, 6·6%), ν(C⁚C) 1673 cm.$^{-1}$.

The amide (0·34 g., 1·61 mmoles), shaken with 40% aqueous sodium hydroxide (25 ml.) for 15 min., gave a mixture (0·23 g., 2·84 mmoles, 88%; *M*, 82·1) of 1,1,2,2-tetrafluoroethane (1·34 mmoles; 83%) and 1,2-difluoroethylene (1·50 mmoles; 93%). Infrared spectroscopy confirmed that these were the only products present.

Reaction of 1,1,2,2-*Tetrafluoroethylphosphine with Ammonia.*—Phosphine (30·3 g., 0·89 mole) and tetrafluoroethylene (89·0 g., 0·89 mole), heated at 150° for 48 hr. in a 1 l.-autoclave, gave 1,1,2,2-tetrafluoroethylphosphine (62·5 g., 0·48 mole; 54%), spectroscopically identical with the sample prepared by the photochemical route.[3]

Ammonia (0·29 g., 16·9 mmoles) and 1,1,2,2-tetrafluoroethylphosphine (0·54 g., 4·0 mmoles), condensed into a 350-ml. Pyrex tube, reacted to give a yellow solid immediately the tube began to warm. When the contents of the tube had attained room temperature, the only volatile product was ammonia (0·066 g., 3·9 mmoles, 23%). The involatile material was washed with water to remove ammonium fluoride, and dried *in vacuo* at room temperature to give the *polymer* $[(CHF_2{\cdot}CH_2{\cdot}P)_3N_2]_n$ (0·31 g.) (Found: C, 23·4; H, 3·0; N, 8·5%. $C_6H_9F_6N_2P_3$ requires C, 22·8; H, 2·9; N, 8·9%). The polymer was only slightly decomposed when heated at 400° for 8 hr. *in vacuo.*

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