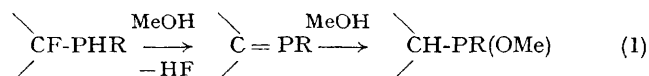


## <sup>19</sup>F and <sup>31</sup>P N.M.R. Characterisation of Phospha-alkene and Phospha-alkyne Intermediates in the Alkaline Hydrolysis of Trifluoromethylphosphine

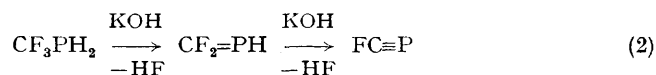
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**Summary** <sup>19</sup>F and <sup>31</sup>P n.m.r. spectroscopy has confirmed the existence of a previously postulated phospha-alkene intermediate in the base hydrolysis of perfluoroalkyl phosphines; a phospha-alkyne intermediate is also formed.

HASZELDINE and his co-workers<sup>1-4</sup> have postulated that the reactions between fluoroalkyl phosphines (R<sub>f</sub>)<sub>n</sub>PH<sub>3-n</sub> (n = 1 or 2), and various bases involve either phospha-alkene intermediates or proceed *via* a hydride shift mechanism, with the former mechanism being preferred, *e.g.* reaction (1).



Previously some of us (H.W.K. and J.F.N.) identified and characterised by microwave spectroscopy<sup>5</sup> several phospha-alkene species R<sup>2</sup>P=CR<sup>1</sup><sub>2</sub> (R<sup>1</sup>=H, R<sup>2</sup>=H; R<sup>1</sup>=F, R<sup>2</sup>=H; R<sup>1</sup>=H, R<sup>2</sup>=Cl) by high temperature pyrolysis reactions of suitable precursors. We now report that the phospha-alkene CF<sub>2</sub>=PH and the phospha-alkyne<sup>6</sup> FC≡P are indeed intermediates in the room temperature reaction (2) between CF<sub>3</sub>PH<sub>2</sub> and solid KOH or NaOEt and we have characterised both species by <sup>19</sup>F and <sup>31</sup>P n.m.r. spectroscopy.



The <sup>31</sup>P{<sup>1</sup>H} n.m.r. spectrum of the products formed when gaseous CF<sub>3</sub>PH<sub>2</sub> is passed rapidly twice through a U-trap containing KOH pellets in a high vacuum system is shown in Figure 1(a). (For convenience and safety the spectra were recorded at *ca.* -80 °C but the compounds show evidence of some stability above this temperature).

The strongest resonance in the <sup>31</sup>P{<sup>1</sup>H} spectrum in Figure 1 is that of unchanged CF<sub>3</sub>PH<sub>2</sub> but the low-field doublet of doublets pattern is exactly that expected for

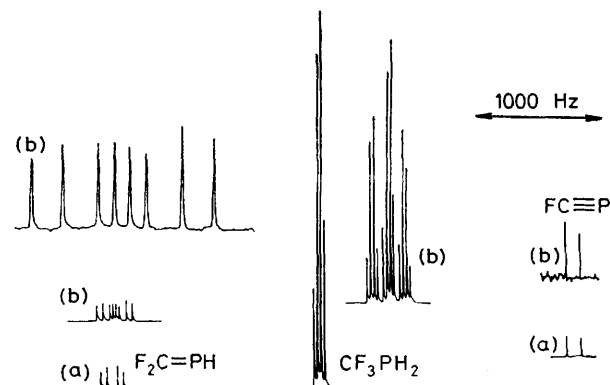


FIGURE 1. <sup>31</sup>P (*ca.* -80 °C) n.m.r. spectra of the products of the reaction (2) between CF<sub>3</sub>PH<sub>2</sub> vapour and solid KOH at room temperature; (a), <sup>1</sup>H decoupled; (b) <sup>1</sup>H undecoupled.

CF<sub>2</sub>=PH and arises from coupling between phosphorus and the two non-equivalent fluorine nuclei F<sup>1</sup> and F<sup>2</sup> (see Table). Furthermore the <sup>1</sup>H-undecoupled <sup>31</sup>P n.m.r.

TABLE. <sup>1</sup>H, <sup>19</sup>F, and <sup>31</sup>P n.m.r. chemical shift and coupling constant data for F<sub>2</sub>C=PH and FC≡P.<sup>a</sup>

		F <sub>2</sub> C=PH		FC≡P	
φ(F <sup>1</sup> )	4.2	δ(P)	-201.4		
φ(F <sup>2</sup> )	-24.6	τ(H)	3.55		
<sup>1</sup> J(PH)	166.6	<sup>3</sup> J(F <sup>1</sup> H)	19.2	<sup>3</sup> J(F <sup>2</sup> H)	40.0
<sup>2</sup> J(PF <sup>1</sup> )	213.6	<sup>2</sup> J(PF <sup>2</sup> )	82.3	<sup>2</sup> J(F <sup>1</sup> F <sup>2</sup> )	25.4
φ(F)	-96.6	δ(P)	-346.4	<sup>2</sup> J(PF)	182.0

<sup>a</sup> <sup>19</sup>F shifts are in p.p.m. relative to CCl<sub>3</sub>F and <sup>31</sup>P shifts in p.p.m. relative to P(OMe)<sub>3</sub> [high-field shifts are negative from Me<sub>4</sub>Si, CCl<sub>3</sub>F, and P(OMe)<sub>3</sub>]. Coupling constants are in Hz. Assignments of F<sup>1</sup> and F<sup>2</sup> are based on a comparison of the magnitudes of <sup>3</sup>J(F<sup>1</sup>H) and <sup>3</sup>J(F<sup>2</sup>H) with the analogous <sup>3</sup>J(FH) data for related fluoroalkenes (J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'Progress in NMR Spectroscopy,' vol. 10, Pergamon, Oxford, 1977).

spectrum [Figure 1(b)] exhibits a further large doublet pattern for all the lines ( $^1J_{\text{FH}} 166.6 \text{ Hz}$ ) from coupling to the single proton directly attached to phosphorus.

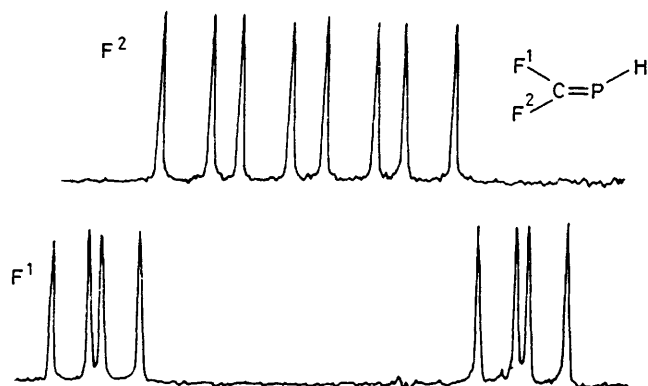


FIGURE 2.  $^{19}\text{F}$  (ca.  $-80^\circ\text{C}$ ) n.m.r. spectrum of  $\text{CF}_2=\text{PH}$ .

In Figure 2 the  $^{19}\text{F}$  n.m.r. spectra of  $\text{CF}_2=\text{PH}$  is shown, exhibiting a total of 16 lines for the two non-equivalent fluorine atoms. The coupling constants obtained agree with those of the phosphorus spectrum.

The  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectrum (Figure 1) also exhibits a weak high-field 1:1 doublet which is unchanged on proton uncoupling and can be assigned to  $\text{FC}\equiv\text{P}$  since the  $^{19}\text{F}$  n.m.r. spectrum reveals a similar doublet of identical  $^2J_{\text{PCF}}$  splitting.

The concentration of  $\text{FC}\equiv\text{P}$  can be increased by extending the contact time of the reactants and can be made quantitative.<sup>6</sup>

I.r. data on the phospho-alkene and phospho-alkyne compounds have been recorded<sup>7</sup> [ $\nu(\text{C}=\text{P}) 1340$ ;  $\nu(\text{C}\equiv\text{P}) 1660 \text{ cm}^{-1}$ ] and fuller details will be published elsewhere.†

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† *Added in proof:* We have recently also characterised the phospho-alkene  $\text{CF}_3\text{P}=\text{CF}_2$  by  $^{19}\text{F}$  and  $^{31}\text{P}$  n.m.r. studies of the reaction between  $(\text{CF}_3)_2\text{PH}$  and  $\text{KOH}$ .

<sup>1</sup> G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J. Chem. Soc.*, 1964, 572.

<sup>2</sup> H. Goldwhite, R. N. Haszeldine, and D. E. Rowsell, *J. Chem. Soc.*, 1965, 6875.

<sup>3</sup> R. N. Haszeldine, D. R. Taylor, and E. W. White, *J. Fluorine Chem.*, 1977, **10**, 27.

<sup>4</sup> R. N. Haszeldine, D. R. Taylor, and E. W. White, *J. Fluorine Chem.*, 1978, **11**, 441.

<sup>5</sup> M. J. Hopkinson, H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, *J.C.S. Chem. Comm.*, 1976, 513.

<sup>6</sup> H. W. Kroto, J. F. Nixon, N. P. C. Simmons, and N. P. C. Westwood, *J. Amer. Chem. Soc.*, 1978, **100**, 446.

<sup>7</sup> R. E. Bear, N. P. C. Simmons, H. E. Hosseini, H. W. Kroto, and J. F. Nixon, unpublished results.