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Preliminary communication

^{19}F AND ^{31}P NMR CHARACTERISATION OF THE PHOSPHAALKENE, $CF_3P{=}CF_2$, INTERMEDIATE IN THE ALKALINE HYDROLYSIS OF BIS(TRIFLUOROMETHYL)PHOSPHINE

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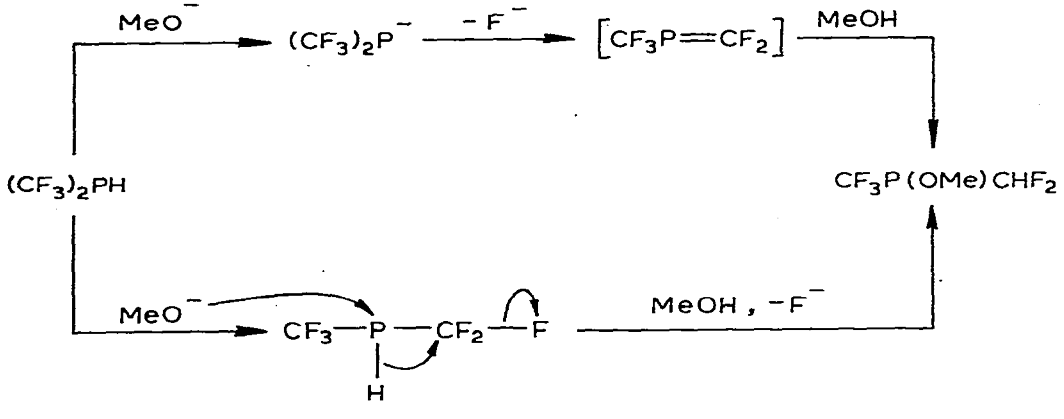
Summary

The previously postulated phosphaalkene intermediate $CF_3P{=}CF_2$ in the alkaline hydrolyses of $(CF_3)_2PH$ has been trapped and characterised by its ^{19}F and ^{31}P NMR spectra.

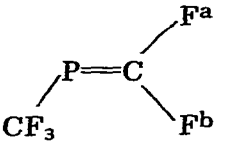
Reactions between primary or secondary polyfluoroalkylphosphines with nucleophiles such as alkoxides and amines [1—5] have been discussed on the basis of either formation of a short lived phosphaalkene intermediate or alternatively involving a nucleophilically initiated hydride ion shift from phosphorus to an α-carbon atom.

Thus in the case of attack of methoxide on $(CF_3)_2PH$ the product $CF_3P(OMe)(CHF_2)$ could arise from the routes shown below:



Previously we have reported the detection by microwave spectroscopy of phosphaalkenes of the type $CF_2{=}PH$, $CH_2{=}PH$ and $CH_2{=}PCl$ from high temperature pyrolysis of suitable phosphine precursors [6,7] and subsequently we have characterised $CF_2=PH$ and $FC\equiv P$ as intermediates in the room temperature base hydrolysis of CF_3PH_2 [8]. Bickelhaupt et al. [9] have recently isolated the stable phosphaalkene (Mes)P=CPh$_2$ (Mes = mesityl) illustrating the importance of steric hindrance to polymerisation in determining the stability of these compounds.

We now report ^{19}F and ^{31}P NMR spectroscopic characterisation of $CF_3P=CF_2$ which confirms the phosphaalkene mechanism for the alkaline hydrolysis of $(CF_3)_2PH$. The $^{31}P\{^1H\}$ NMR spectrum at −78°C of the products formed when gaseous $(CF_3)_2PH$ is passed several times through a U-trap containing KOH pellets in a high vacuum line is shown in Fig. 1. The high field resonance is of unreacted $(CF_3)_2PH$ ($^2J(PF)$ 65.9 Hz) [10].



(I)

The low field resonance is that expected for the phosphaalkene intermediate $CF_3P=CF_2$ (I) consisting of an overlapping doublet of doublets of quartets from spin-coupling to F^a, F^b and the CF_3 group. Chemical shift and coupling constant data are listed in Table 1.

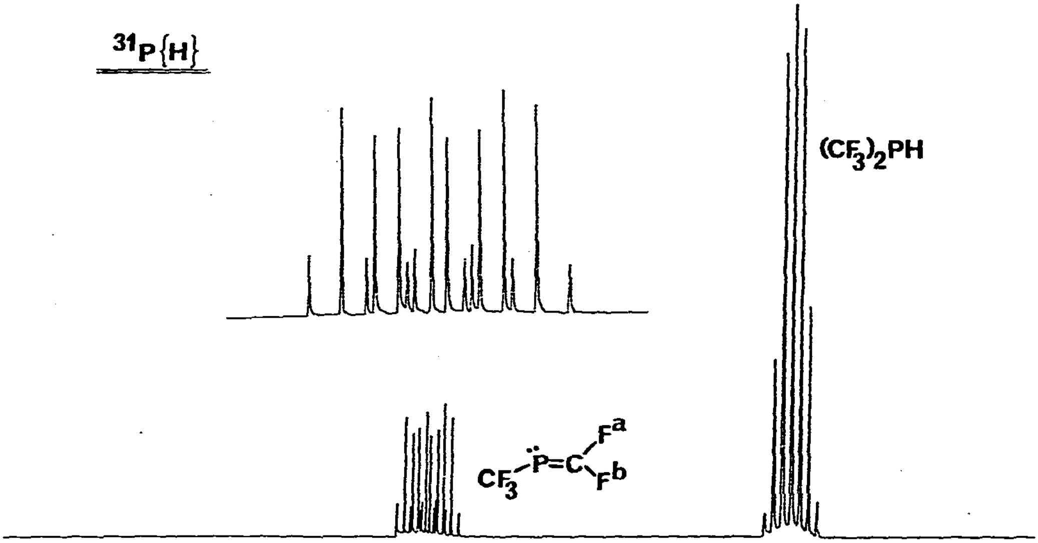


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum at −78°C of the products of the reaction between $(CF_3)_2PH$ and KOH.

TABLE 1

SOME NMR DATA FOR PHOSPHAALKENES

	$\delta(P)^a$	$\varphi(F^a)^b$	$\varphi(F^b)^b$	$J(PF^a)^c$	$J(PF^b)^c$	$J(F^aF^b)^c$	Ref.
$CF_2=PH$	−201.4	4.2	−24.6	213.6	82.3	25.4	[8]
$CF_2=PCF_3$	−121.4	3.9	−38.7	191.4	103.9	29.3	This work

^{a}Rel. $P(OMe)_3$. ^{b}Rel. CCl_3F. ^{c}In Hz.

The ^{19}F NMR spectrum of the products confirms the assignments, and in addition reveals the presence of both CF_3H (doublet ^2J(FH) 79.4 Hz) and CF_2H_2 (triplet ^2J(FH) 50.1 Hz). These products are expected to result from addition of water across the double bond of the phosphaalkene followed by normal alkali cleavage of the fluoro-carbon substituents of the resulting phosphine viz.

$$CF_3P{=}CF_2 \xrightarrow{H_2O} CF_3P(OH)CF_2H \xrightarrow{OH^-} \left.\begin{array}{l} CF_3H \\ CF_2H_2 \end{array}\right\}$$

Acknowledgement

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