

^{31}P , ^{19}F AND ^1H NMR SPECTROSCOPIC STUDY OF THE REACTION OF BIS(TRIFLUOROMETHYL)PHOSPHINE AND SOLID KOH. SYNTHESIS OF THE PHOSPHAALKENE $\text{CF}_3\text{P}=\text{CF}_2$

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Summary

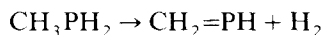
The formation and subsequent reaction of the phosphalkene $\text{CF}_3\text{P}=\text{CF}_2$ obtained via dehydrofluorination of $(\text{CF}_3)_2\text{PH}$ with KOH pellets at room temperature has been studied by multinuclear NMR spectroscopy.

Introduction

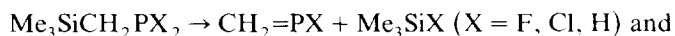
There is considerable current interest in compounds containing multiple bonds between carbon and tervalent phosphorus [1,2] and a large number of stable phosphalkenes $\text{R}_2\text{C}=\text{PX}$ which violate the "double bond rule" have now been established.

The simpler members of this class of compounds are of course much less stable (e.g. $\text{CH}_2=\text{PX}$; $\text{X} = \text{Cl}, \text{H}, \text{F}$ [3–7] and $\text{CF}_2=\text{PH}$ [3,8]), but can be detected spectroscopically and their molecular geometry established by microwave studies.

Previously we have utilised a variety of synthetic routes for phosphalkenes e.g. (i) thermal elimination of H_2 , CH_4 and hydrogen halides from simple organophosphines, e.g.:



(ii) Use of trimethylsilylmethylphosphine precursors [9], e.g.:



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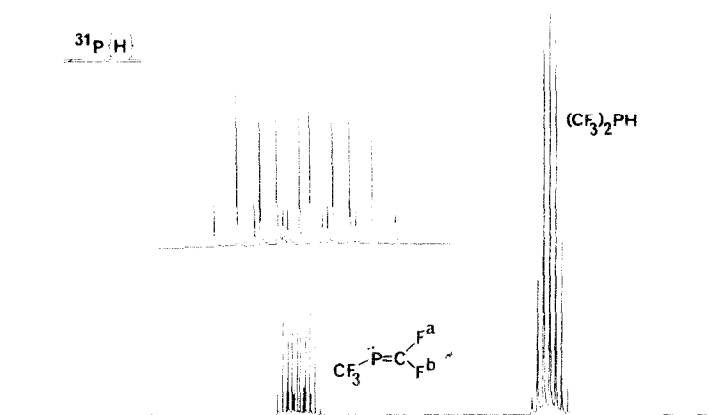


Fig. 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at -78°C of the products of the reaction between $(\text{CF}_3)_2\text{PH}$ and KOH .

(iii) base induced dehydrofluorination of trifluoromethyl phosphine at room temperature:

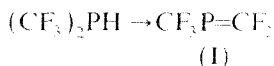


We now describe extension of the dehydrofluorination approach to the synthesis of $\text{CF}_3\text{P}=\text{CF}_2$ [23].

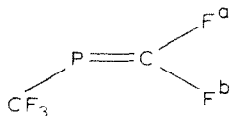
Results and discussion

The availability of ^1H , ^{19}F and ^{31}P nuclei ($I = 1/2$, 100% abundant) makes NMR spectroscopy an ideal method of studying intermediates and products of the reaction between $(\text{CF}_3)_2\text{PH}$ and KOH . Figure 1 shows the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at -78°C of the products formed when gaseous $(\text{CF}_3)_2\text{PH}$ is allowed to evaporate slowly from -196°C to room temperature and is passed several times through a U-trap containing KOH pellets held at room temperature in the high vacuum manifold.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum confirms that a dehydrofluorination reaction has readily occurred even under these mild conditions to afford the novel phosphalkene $\text{CF}_3\text{P}=\text{CF}_2$ (I) viz.:



The ^{31}P resonance of I is that expected for the structure: in which there is no



rapid rotation about the $\text{P}=\text{C}$ double bond, and consists of a 16 line pattern formed by the overlapping of a doublet ($^2J(\text{PF}^a)$) of doublets ($^2J(\text{PF}^b)$) of 1-3-3-1 quartets ($^2J(\text{PCF})$). Chemical shift and spin-spin coupling constant data are listed in Table 1.

TABLE 1
CHEMICAL SHIFT AND COUPLING CONSTANT DATA (Hz) FOR $\text{CF}_3\text{P}=\text{CF}_2$ (I)

Compound	$\delta(\text{P})^a$	$\Phi(\text{F}^a)$	$\Phi(\text{F}^b)^b$	$\Phi(\text{CF}_3)^b$	$J(\text{PCF}_3)$	$J(\text{PF}^a)$	$J(\text{PF}^b)$
$\text{CF}_3\text{P}=\text{CF}_2$	-121.4	-28.7	+3.9	-44.0	59.5	191.4	103.9
	$J(\text{F}^a\text{CF}_3)$	$J(\text{F}^b\text{CF}_3)$	$J(\text{F}^a\text{F}^b)$				
	18.0	9.3	29.3				

^a In ppm rel. H_3PO_4 . ^b In ppm rel. CCl_3F .

Further confirmation of the structural assignment comes from the proton undecoupled ^{31}P NMR spectrum (Fig. 2) in which the resonance of I remains unchanged whereas the highfield septet assigned to the presence of unreacted $(\text{CF}_3)_2\text{PH}$ in Fig. 1 ($^2J(\text{PF})$ 65.9 Hz) becomes a doublet of septets in Fig. 2 ($^1J(\text{PH})$ 225.6 Hz). The IR spectrum of $\text{CF}_3\text{P}=\text{CF}_2$ has been reported elsewhere by Burg [10] who obtained the compound via a different synthetic approach.

The simplicity of the ^{31}P NMR spectra does not however reveal the true complexity of the reaction between $(\text{CF}_3)_2\text{PH}$ and KOH which is more fully established by the ^1H and ^{19}F NMR spectra of the same reaction mixture.

The ^{19}F NMR spectrum of the reaction products consists mainly of resonances (i)–(vi) which are shown in expansion in Fig. 3. Resonances (i)–(iii) can be readily assigned as arising from $\text{CF}_3\text{P}=\text{CF}_2$ (I) consisting of a doublet of doublets of quartets (F^a), a doublet of doublets of quartets (F^b) and a doublet of doublets of doublets (CF_3). Chemical shift $\Phi(\text{F})$ and coupling constant data are listed in Table 1. Resonance (iv) which consists of a doublet of doublets ($\Phi(\text{F})$ 47.3 ppm, $^2J(\text{PF})$ 65.9 Hz $^3J(\text{FH})$ 9.8 Hz) is due to the unreacted $(\text{CF}_3)_2\text{PH}$ [11,12].

Of special interest are resonances (v) and (vi) which occur as a doublet and triplet pattern respectively and can be readily assigned to CF_3H ($\Phi(\text{F})$ 77.8 ppm, $^2J(\text{FH})$ 80.6 Hz) (cf. lit. [13,14] $\Phi(\text{F})$ 76.0 ppm, $^2J(\text{FH})$ 79.7 Hz) and CF_2H_2 , respectively,

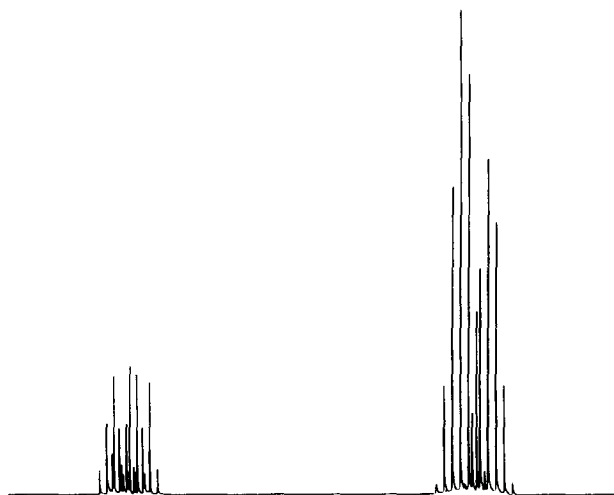


Fig. 2. ^{31}P proton undecoupled spectrum of I.

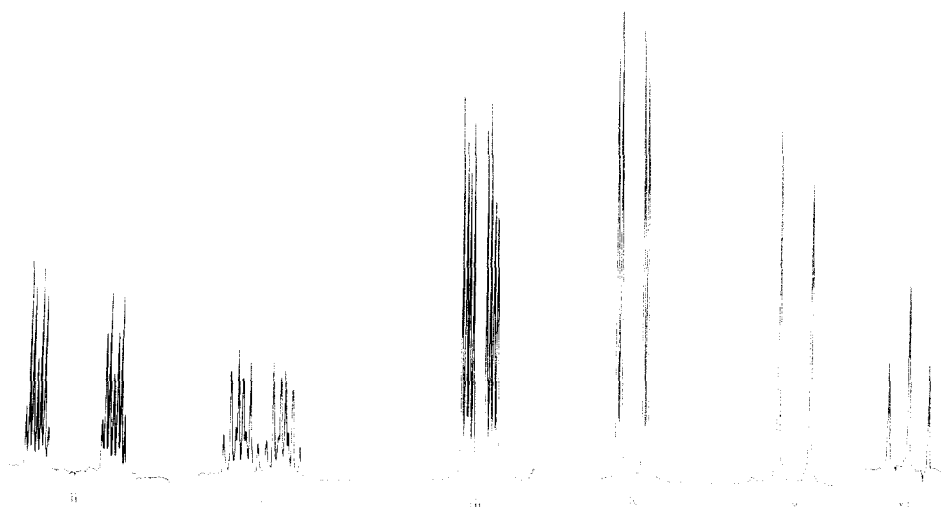


Fig. 3. ^{19}F NMR spectrum of reaction products.

($\Phi(\text{F})$ 142.1 ppm, $^2J(\text{FH})$ 50.1 Hz (cf. lit. [14,15] $\Phi(\text{F})$ 143 ppm, $^2J(\text{FH})$ 50.2, 50.4 Hz). These latter products result from base induced cleavage of the P-C bonds and the CF_3H which is in greatest amount can arise from both $(\text{CF}_3)_2\text{PH}$ and $\text{CF}_3\text{P}=\text{CF}_2$. The origin of CF_3H_2 must presumably result from the cleavage of a P- CF_2H bond and it seems likely that water present in the solid KOH has added across the double bond of I to yield $(\text{CF}_3)(\text{CF}_2\text{H})\text{POH}$ which then undergoes P-C cleavage.

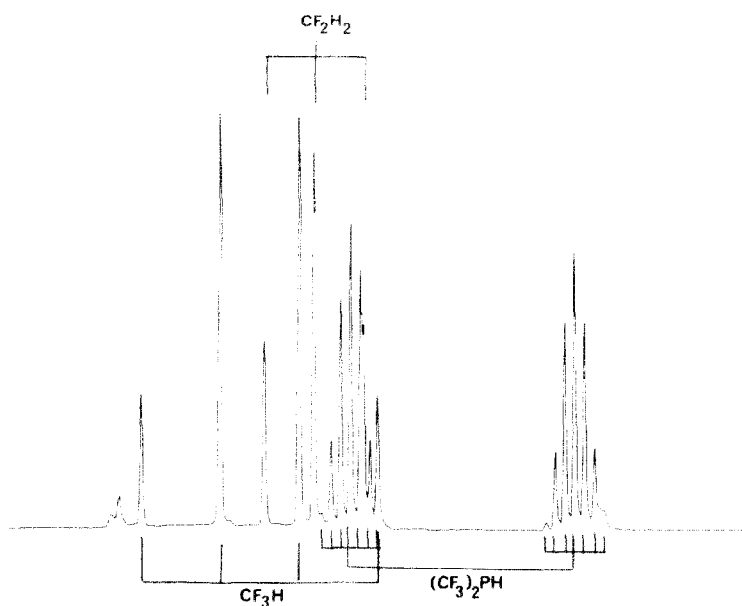
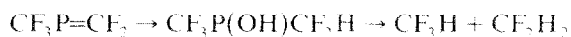


Fig. 4. ^1H NMR spectrum of reaction products.

This would be analogous to the addition of alcohols or amines to short lived phosphalkene intermediates first proposed by Haszeldine and coworkers [16–20] to explain the products of reactions between primary or secondary polyfluoroalkylphosphines and nucleophiles.

The ^1H NMR spectrum of the reaction products (Fig. 4) provides further confirmation of the formation of CF_3H and CF_2H_2 exhibiting the expected 1-3-3-1 quartet and 1-2-1 triplet pattern both partially overlapping the septet pattern of the unreacted $(\text{CF}_3)_2\text{PH}$. Interestingly no evidence was found for any significant formation of the cyclic dimer or trimer of I $(\text{CF}_3\text{PCF}_2)_n$ ($n = 2, 3$), under these reaction conditions although both these species have been observed by Burg [10] in the base-catalysed dehydrofluorination of $(\text{CF}_3)_2\text{PH}$ with ZnMe_2 . Very recently Grobe and Le Van [21] have observed these species from polymerisation of $\text{CF}_3\text{P}=\text{CF}_2$ synthesised quantitatively by the high temperature pyrolysis of $\text{Me}_3\text{SnP}(\text{CF}_3)_2$.

Experimental

Bis(trifluoromethyl)phosphine was prepared by PH_3 reduction of $(\text{CF}_3)_2\text{PI}$ [22] and carefully purified by trap to trap fractionation in the high vacuum manifold. Its identity was confirmed by its molecular weight and characteristic infrared spectrum.

NMR spectra were recorded on a JEOL PFT 100 spectrometer operating at 100 MHz for ^1H , 94.00 MHz for ^{19}F and 40.44 MHz for ^{31}P .

Acknowledgement

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