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^{31}P, ^{19}F AND ^{1}H NMR SPECTROSCOPIC STUDY OF THE REACTION OF BIS(TRIFLUOROMETHYL)PHOSPHINE AND SOLID KOH. SYNTHESIS OF THE PHOSPHAALKENE $CF_3P{=}CF_2$

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Summary

The formation and subsequent reaction of the phosphaalkene $CF_3P{=}CF_2$ obtained via dehydrofluorination of $(CF_3)_2PH$ 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 phosphaalkenes $R_2C{=}PX$ 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. $CH_2{=}PX$; $X = Cl$, H, F [3–7] and $CF_2{=}PH$ [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 phosphaalkenes e.g. (i) thermal elimination of H_2, CH_4 and hydrogen halides from simple organophosphines, e.g.:

$$(CH_3)_2PH \rightarrow CH_2{=}PH + CH_4$$

$$CH_3PH_2 \rightarrow CH_2{=}PH + H_2$$

$$CH_3PCl_2 \rightarrow CH_2{=}PCl + HCl$$

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

$$Me_3SiCH_2PX_2 \rightarrow CH_2{=}PX + Me_3SiX\ (X = F, Cl, H)\ \text{and}$$

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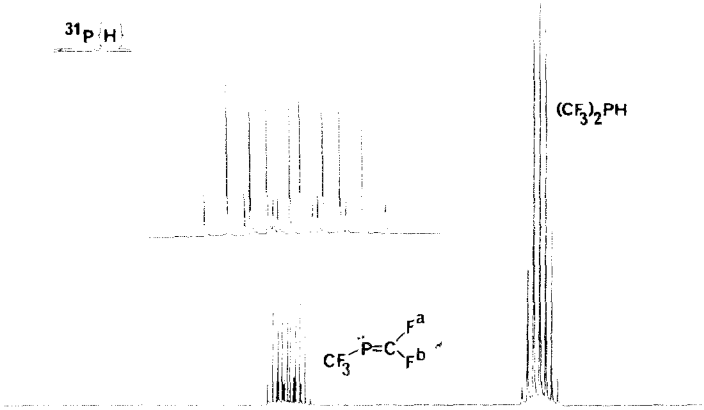


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum at −78°C of the products of the reaction between $(CF_3)_2PH$ and KOH.

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

$$CF_3PH_2 \xrightarrow{KOH} CF_2{=}PH$$

We now describe extension of the dehydrofluorintation approach to the synthesis of $CF_3P{=}CF_2$ [23].

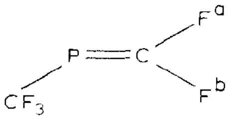
Results and discussion

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 $(CF_3)_2PH$ and KOH. Figure 1 shows the $^{31}P\{^1H\}$ NMR spectrum at −78°C of the products formed when gaseous $(CF_3)_2PH$ 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 $^{31}P\{^1H\}$ NMR spectrum confirms that a dehydrofluorination reaction has readily occurred even under these mild conditions to afford the novel phosphaalkene $CF_3P{=}CF_2$ (I) viz.:

$$(CF_3)_2PH \rightarrow \underset{(I)}{CF_3P{=}CF_2}$$

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



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

TABLE 1

CHEMICAL SHIFT AND COUPLING CONSTANT DATA (Hz) FOR $CF_3P{=}CF_2$ (I)

Compound	$\delta(P)$ [a]	$\Phi(F^a)$	$\Phi(F^b)$ [b]	$\Phi(CF_3)$ [b]	$J(PCF_3)$	$J(PF^a)$	$J(PF^b)$
$CF_3P{=}CF_2$	−121.4	−28.7	+3.9	−44.0	59.5	191.4	103.9
	$J(F^aCF_3)$	$J(F^bCF_3)$	$J(F^aF^b)$				
	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 $(CF_3)_2PH$ in Fig. 1 ($^2J(PF)$ 65.9 Hz) becomes a doublet of septets in Fig. 2 ($^1J(PH)$ 225.6 Hz). The IR spectrum of $CF_3P{=}CF_2$ 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 $(CF_3)_2PH$ 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 $CF_3P{=}CF_2$ (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 $\Phi(F)$ and coupling constant data are listed in Table 1. Resonance (iv) which consists of a doublet of doublets ($\Phi(F)$ 47.3 ppm, $^2J(PF)$ 65.9 Hz $^3J(FH)$ 9.8 Hz) is due to the unreacted $(CF_3)_2PH$ [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 ($\Phi(F)$ 77.8 ppm, $^2J(FH)$ 80.6 Hz) (cf. lit. [13,14] $\Phi(F)$ 76.0 ppm, $^2J(FH)$ 79.7 Hz) and CF_2H_2, respectively,

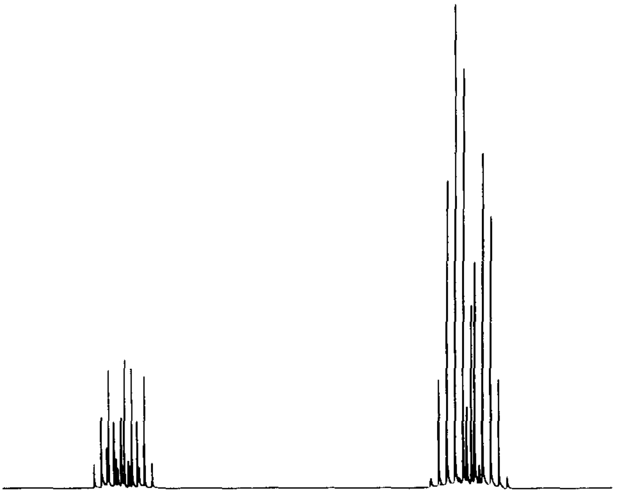


Fig. 2. ^{31}P proton undecoupled spectrum of I.

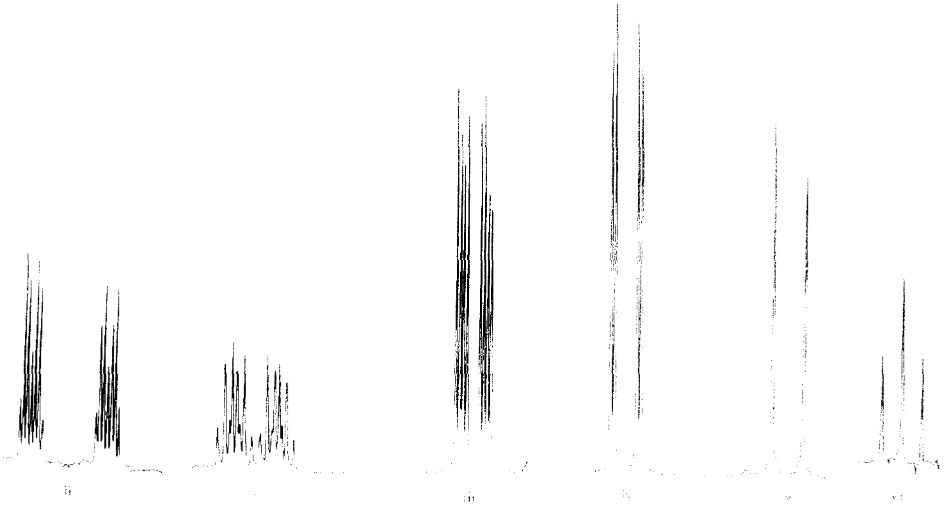


Fig. 3. ^{19}F NMR spectrum of reaction products.

(Φ(F) 142.1 ppm. ^2J(FH) 50.1 Hz (cf. lit. [14,15] Φ(F) 143 ppm. ^2J(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 $(CF_3)_2PH$ and $CF_3P{=}CF_2$. The origin of CF_2H_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 $(CF_3)(CF_2H)POH$ which then undergoes P–C cleavage.

$$CF_3P{=}CF_2 \rightarrow CF_3P(OH)CF_2H \rightarrow CF_3H + CF_2H_2$$

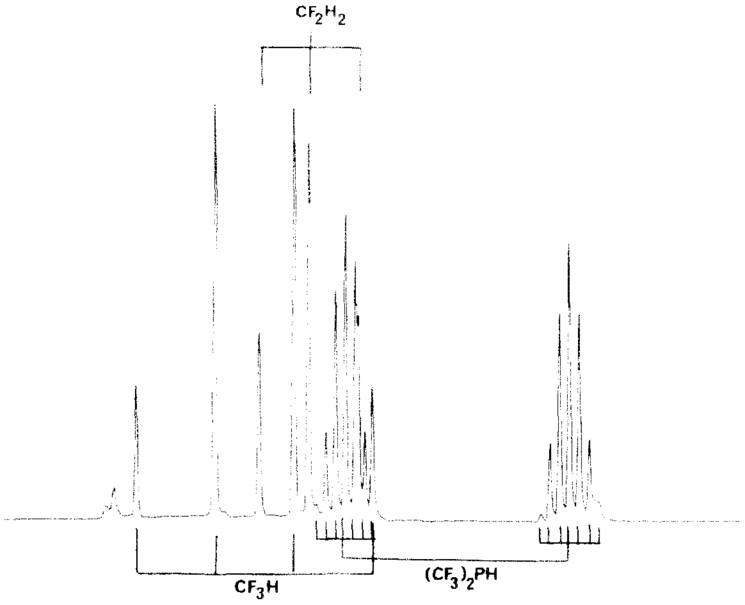


Fig. 4. ^{1}H NMR spectrum of reaction products.

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

The ^{1}H 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 $(CF_3)_2PH$. Interestingly no evidence was found for any significant formation of the cyclic dimer or trimer of I $(CF_3PCF_2)_n$ ($n = 2, 3$), under these reaction conditions although both these species have been observed by Burg [10] in the base-catalysed dehydrofluorination of $(CF_3)_2PH$ with $ZnMe_2$. Very recently Grobe and Le Van [21] have observed these species from polymerisation of $CF_3P{=}CF_2$ synthesised quantitatively by the high temperature pyrolysis of $Me_3SnP(CF_3)_2$.

Experimental

Bis(trifluoromethyl)phosphine was prepared by PH_3 reduction of $(CF_3)_2PI$ [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 ^{1}H, 94.00 MHz for ^{19}F and 40.44 MHz for ^{31}P.

Acknowledgement

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