Journal of Fluorine Chemistry, 56 (1992) 385–388

Preliminary Note

Metaphosphate intermediates from fluoroaromatic precursors*

Richard D. Chambers, Keith B. Dillon and Thomas A. Straw
Chemistry Department, University of Durham, South Road, Durham, DH1 3LE (UK)

(Received September 24, 1991; accepted November 2, 1991)

Abstract
Flow pyrolysis of some 2-aryloxy-1,3,2-dioxaphospholanes with *ortho*-CF_3 or F substituents, either alone or in the presence of methanol, has provided evidence for the formation of metaphosphates as intermediates; these highly reactive species then undergo further reaction, depending on the nature of the substituent. Mass spectrometric studies of the starting materials have also suggested the elimination of ethylene and the formation of metaphosphates to a limited extent.

Introduction

Cadogan, Gosney and co-workers have described the generation of aryl metaphosphate derivatives in the gas phase by flash vacuum pyrolysis of 2-aryloxy-1,3,2-dioxaphospholanes [1, 2]. The intermediate metaphosphate species were clearly extremely electrophilic, and were not isolated. Instead, either an intramolecular insertion of the phosphorus into a C−H bond occurred, giving a practical route to phosphonic acids after work-up, or β-hydrogen abstraction took place to form a terminal alkene by loss of HPO_3 [1, 2]. Even when the *ortho* position of the phenyl ring was blocked by a Bu^t group, insertion into one of the methyl groups was observed. The possibility then arises, however, of blocking the *ortho* positions with other suitable groups such as F or CF_3, which could lead to better prospects of isolating a metaphosphate species. Here we report preliminary findings from flow pyrolysis experiments on an $Ar_FP(OCH_2)_2$ where Ar_F is an aromatic group with F or CF_3 groups in the *ortho* position.

Experimental

Except where indicated otherwise, manipulations were carried out either under an inert atmosphere of dry nitrogen or *in vacuo*. Ethylene chlorophosphite, $P(Cl)(OCH_2)_2$ was prepared from PCl_3 and ethylene glycol by the

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*Dedicated to Professor Alois Haas, with our very best wishes, on the occasion of his 60th birthday

0022-1139/92/$5.00

method of Lucas *et al.* [3] (^{31}P NMR (CH_2Cl_2) δ: 167.0 ppm; lit. value [4]: 167 ppm). The 2-aryl-1,3,2-dioxaphospholanes were synthesised by reaction of ethylene chlorophosphite with either 2,6-$(CF_3)_2C_6H_3Li \cdot$TMEDA or C_6F_5MgBr at 195 K in Et_2O, according to the method of Mukaiyama and co-workers [5]. The compounds were characterised after isolation by elemental analysis for C and H, mass spectrometry, and ^{31}P and ^{19}F NMR spectroscopy. Selected NMR data: (**1**) (Ar=2,6-$(CF_3)_2C_6H_3$): ^{31}P NMR (CH_2Cl_2) δ: 155.9 (septet, $J_{PF}=35.1$ Hz) ppm. ^{19}F NMR δ: -55.4 (d, $J_{PF}=35.1$ Hz) ppm. (**2**) (Ar=C_6F_5): ^{31}P NMR (CH_2Cl_2) δ: 146.5 ppm. ^{19}F NMR δ: -137.4 (2F); -153.6 (1F); -163.9 (2F) ppm.

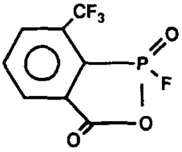
The pyrolyses were carried out using a nitrogen flow technique developed in Durham for ethylene elimination from fluorocarbon systems [6], with a vertically mounted quartz pyrolysis tube containing loosely packed glass wool, a dropping funnel and nitrogen inlet tap at the top, and a system of traps at the bottom. Material for pyrolysis was dripped into the tube heated to 713 K, and vapour was carried through the tube by the flow of nitrogen; product(s) from ethylene elimination were collected in the first trap, cooled to 195 K (cardice) and gaseous products such as ethylene passed into a second, liquid nitrogen-cooled trap. The nitrogen flow was set at c. 220 cm^3 min^{-1}, and, by adding one drop of material every minute to the tube, (vol. *c.* 150 cm^3), it was intended that the vapour produced from each addition should have completely passed down the column before the following drop was added, thus minimising reaction of pyrolysis products with the starting materials. The 2-aryl-1,3,2-dioxaphospholanes were low-melting solids, which were liquidified by gently warming the dropping funnel with a heat gun. In general, only a small amount of charring was observed in the tube, and, after taking into account any elimination of ethylene, the yield (by mass) of the pyrolysis products recovered was always over 80%.

^{31}P NMR shifts are quoted relative to external 85% H_3PO_4 and ^{19}F shifts relative to $CFCl_3$, with the high-frequency (lower field) direction taken as positive. Spectra were recorded on a Bruker AC250 instrument at 101.256 (^{31}P) and 235.360 (^{19}F) MHz, respectively. Mass spectra were obtained using a Ribermag R10 10E or VG 707E instrument incorporating a Hewlett-Packard 5790A gas chromatograph, fitted with a 25 m crosslinked methyl silicone capillary column. Perfluorokerosene was used for referencing.

Results and discussion

(a) Reactions of 2,6-$(CF_3)_2C_6H_3P(OCH_2)_2$ (1)

Pyrolysis of **1** (2 g) yielded a white waxy solid (1.4 g), which NMR analysis showed to contain a mixture of two phosphorus compounds, in an approximately 9:1 ratio of signal intensities. The NMR data were quite revealing. The major product (**3**) gave a doublet in its ^{31}P spectrum (^{31}P NMR 9.05 ppm; $^1J_{PF}=1117$ Hz), and two sets of resonances in its ^{19}F spectrum, a doublet at -67.6 ppm [$^1J_{PF}=1117$ Hz (1F)] and a singlet at -67.8 ppm (3F). These results clearly indicate a single CF_3 group, and an F directly bonded to P. The ^{1}H NMR spectrum showed only aromatic protons, and demonstrated that ethylene had been entirely lost from the system. Furthermore, mass spectra (EI^+) showed a mass ion at *m/e* 254, together with *m/e* 235 (M−F) and 210 ($M-CO_2$). The structure compatible with all of these data is:



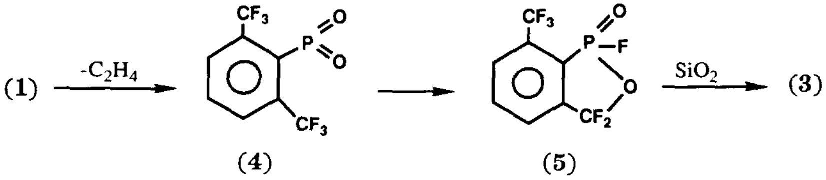
(3)

Formation of **3** is consistent with the intermediate generation of a metaphosphate **4**, followed by insertion into a C−F bond (Scheme 1). The α-haloether **5** is obviously vulnerable to the loss of fluorine, however, and this probably occurs by reaction with silica at the high temperature of the reactor. This reaction provides a further example of the extreme electrophilicity of the metaphosphate, and an indication of the limitations of CF_3 as a blocking group. The minor product of this reaction gave a triplet in the ^{31}P NMR spectrum (δ 0.79 ppm; $^1J_{PF}=1115$ Hz), and was clearly of the form $RP(O)F_2$, though the exact nature of R could not be established because of its low concentration.

The mass spectrum of **1** (CI^-) showed mainly the aryl anion $[2,6\text{-}(CF_3)_2C_6H_3]^-$ (*m/e* 213, 100%) as well as peaks from the mass ion (*m/e* 304) and $(M-1)^+$, but notably two peaks at *m/e* 276 and 277, corresponding to the metaphosphate $[2,6\text{-}(CF_3)_2C_6H_3PO_2]^-$ and its protonated form, respectively.

(b) *Reactions of $C_6F_5P(OCH_2)_2$ (2)*

The pentafluorophenyl compound **2** gave a complex mixture of products when pyrolysed alone, as shown by numerous broad signals in both the ^{31}P and ^{19}F NMR spectra. In contrast, co-pyrolysis with methanol gave the phosphinic acid $C_6F_5P(O)H(OH)$ (**6**), together with, rather surprisingly, ethylene glycol, in a *c.* 1:1 molar ratio. Compound **6** was identified by NMR spectral analysis (^1H NMR δ: 7.76 ppm; d; $^1J_{PH}=630$ Hz; ^{31}P NMR δ: 5.3 ppm; d; $^1J_{PH}=630$ Hz), as was the ethylene glycol. Mechanisms involving a metaphosphate intermediate can be envisaged for this reaction, but direct evidence is lacking.



Scheme 1.

A mass spectrometric study of **2** by electronic ionisation (EI^+) was conducted to explore the potential elimination of ethylene, and showed major peaks at *m/e* 91 (100%) assigned to $[P(O_2C_2H_4)]^+$, 258 (60%) corresponding to $[M^+]$, and 259 (40%) corresponding to $[M+1]^+$. A minor peak was also observed at *m/e* 230, compatible with the loss of ethylene and the formation of the metaphosphate. There was no evidence for fragmentation involving elimination of ethylene under chemical ionisation (CI^+), with ammonia as the ionising agent. In the negative mode (CI^-), however, the largest peak was from $[C_6F_5]^-$ at *m/e* 167, while, surprisingly, the next largest peak was at 381, probably from $[(C_6F_5)_2PO]^-$, suggesting a bimolecular displacement by $[C_6F_5]^-$ inside the mass spectrometer; minor peaks at 230 and 231 were observed, indicating that $[C_6F_5PO_2]^-$ and $[C_6F_5PO_2H]^-$ might be formed by the elimination of ethylene, but not as a major fragmentation process.

We thus conclude that the metaphosphate species can be formed by elimination of ethylene from 2-aryloxy-1,3,2-dioxaphospholanes with *o*-fluoro or *o*-trifluoromethyl substituents on the aromatic ring, either under flow pyrolysis conditions or inside the mass spectrometer. In the pyrolysis experiments, however, the highly reactive metaphosphate reacts further to give products which depend on the nature of the substituent and/or any agent of co-pyrolysis. Further experiments on these and related systems are in progress.

Acknowledgements

We thank Dr I. Gosney (University of Edinburgh) for helpful discussions, and the S.E.R.C. for the award of a maintenance grant (to T.A.S.).

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