

Formation of an unusual mixed boric–phosphinic acid ester derived from perfluoropinacol

Othmar Stelzer^a, Matthias Volkholz^a, Reinhard Schmutzler^{b,*}

^aFachbereich 9, Anorganische Chemie, Bergische Universität-GH Wuppertal, Gausstrasse, 20, D-42097 Wuppertal, Germany

^bInstitut für Anorganische und Analytische Chemie der Technischen Universität, P.O. Box 3329, D-38023, Braunschweig, Germany

Received 16 July 2001; accepted 31 August 2001

Dedicated to Professor Karl Christe on the occasion of his 65th birthday

Abstract

On treatment of the Me₃Si-functional 1,3,2σ⁵λ⁵-dioxaphospholane (**1**) with boron trichloride the novel mixed boric–phosphinic acid ester (**3b**) of perfluoropinacol is formed in a ring-opening reaction, instead of the expected mixed anhydride (**3a**) with pentavalent phosphorus. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Mixed anhydrides; 1,3,2σ⁴λ⁵-Dioxaphospholane; Ring opening; Mixed boric–phosphinic acid ester

1. Introduction

Trimethylsiloxy-substituted phosphoranes have been synthesized first by Cavell et al. [1] and then by Ramirez et al. [2] by addition of hexamethyldisiloxane to (CF₃)₃PO or in the reaction of spirobis-catecholchlorophosphorane with trimethylsilanol, respectively. The reaction of hexafluoroacetone with Me₂P–O–SiMe₃ was found to afford the trimethylsiloxy phosphorane **A** (= **1**) (X = OSiMe₃) [3] (see Scheme 1). Such compounds, involving pentacoordinate phosphorus and containing trimethylsiloxy groups, are versatile starting materials for the synthesis of functionalized phosphoranes as shown by us before [3]. In addition to chloro, fluoro, amino, methoxy and azido derivatives **A** even anhydrides of acids with pentacoordinated phosphorus, e.g. **B** [4], have been synthesized using this method. All these compounds are derived from hexafluoroacetone, the inorganic chemistry of which has been reviewed by Roesky and coworkers [5].

Few anhydrides of pentavalent phosphorus acids are known [6,7]. On oxidation of 1,2-dimethyl-1,2-diphospholane by tetrachloro-*o*-benzoquinone the anhydride **C** was obtained [8]. Allcock et al. [9] reported compounds related to **B** containing σ⁵λ⁵P–NH–σ⁵λ⁵P bridges instead of σ⁵λ⁵P–O–σ⁵λ⁵P units. Mixed anhydrides between acids of trivalent phosphorus and boric acid, e.g.

Me_{*n*}B(O–P(CF₃)₂)_{3–*n*} (*n* = 0–2) were synthesized by Burg and Basi in the 1960ies [10,11].

2. Results and discussion

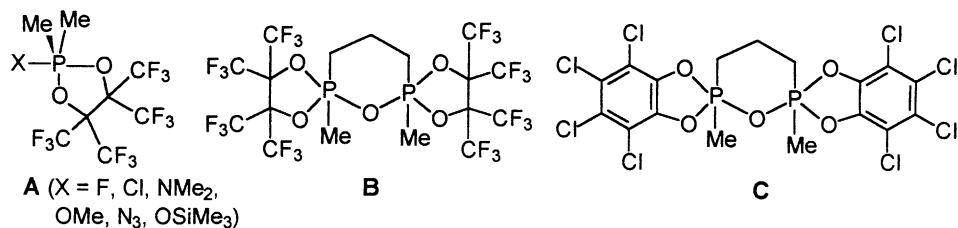
In analogy with the formation of the anhydride (**2a**) according to (Eq. (1) (see Scheme 2) we expected the reaction of **1** with boron trichloride in a 3:1 stoichiometric ratio to give the mixed anhydride **3a** of 1,3,2σ⁵λ⁵-dioxaphospholane-2-ol with pentavalent phosphorus and boric acid (Eq. (3) in Scheme 2). The product **3b** thus obtained showed the correct elemental analysis and the mass spectrum displayed a peak for the molecular ion at *m/e* = 1238, as expected for **3a**. However, the ³¹P{¹H} NMR spectrum revealed a singlet at δP = 61.2 ppm in a shift range typical of phosphinic acid esters R₂P(=O)OR' [12]. For the starting material **1** and the related methoxyphosphorane **A**(X = OMe) with pentacoordinated phosphorus δP values of –2.0 and –8.5 ppm were observed. The δP value of the reaction product thus indicated that the phospholane ring system was opened during the reaction, the mixed boric–phosphinic acid ester (**3b**) of 2,3-bis(trifluoromethyl)-1,1,1,4,4,4-hexafluoro-2,3-butanediol (perfluoropinacol) being formed.

This interpretation of the ³¹P NMR shift of **3b** is supported by the observation of two resonances for the CF₃ groups at δF = –68.6 and –70.0 ppm in the ¹⁹F NMR spectrum. In the case of a phosphorane structure **3a** of the reaction product only one ¹⁹F NMR resonance would be expected,

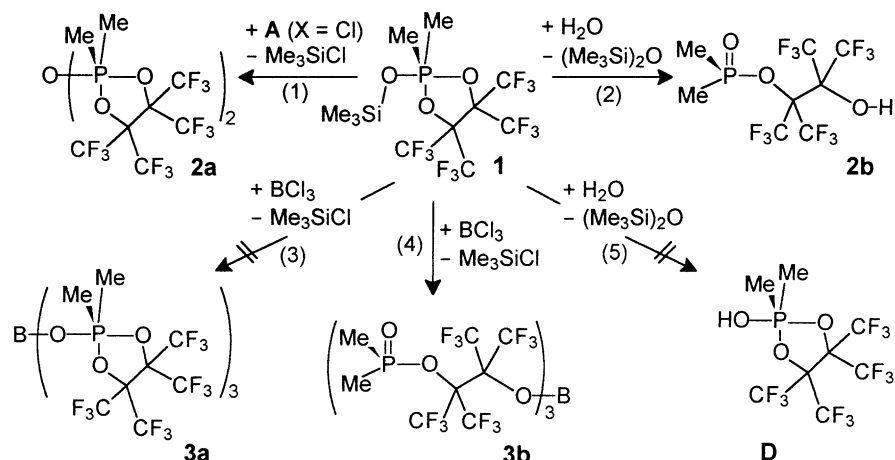
* Corresponding author. Tel.: +49-531-391-5304;

fax: +49-531-391-5387.

E-mail address: r.schmutzler@tu-bs.de (R. Schmutzler).



Scheme 1.



Scheme 2.

since the four CF₃ groups are equivalent on the NMR time scale due to rapid intramolecular ligand exchange processes. This was demonstrated for the compounds of type **A** (X = Cl, F, NMe₂, N₃, OMe) and the starting compound **1** [3], all of which show only one resonance for the CF₃ groups in the ¹⁹F NMR spectrum at ambient temperature. For the fluoro and chloro derivatives of type **A**, however, two resonances are observed at –80 °C in the ¹⁹F NMR spectrum.

The reaction of **1** with BCl₃, apparently, proceeds in an analogous manner as the hydrolysis of **1** (Eq. (2) in Scheme 2) which did not give the expected hypothetical hydroxyphosphorane **D** (Scheme 2), but rather, the phosphinic ester (**2b**) with an open-chain structure comparable to that of its boric acid ester derivative (**3b**). This is strongly supported by the almost identical δF values for the CF₃ groups in both compounds (**2b**: $\delta F = -68.5$ and -70.0 ppm) and the similar δF values in different solvents (**2b**: 61.5 (ethanol) [13], 68.5 (CHCl₃) [3], **3b**: 61.2 ppm). The structure of **2b** has been proved by X-ray structural analysis [13] showing a dimeric arrangement with strong O–H···O hydrogen bridges between the two molecules.

3. Experimental

3.1. General

¹⁹F NMR and ³¹P{¹H} NMR spectra were recorded on a JEOL C 60 HL and Varian XL 100 spectrometer,

respectively, mass spectra on a Varian MAT 311 A instrument. Compound **1** was prepared according to the literature [3].

3.2. Synthesis of **3b**

To a solution of 3.14 g (6.5 mmol) of **1** in 15 ml of dichloromethane, placed in a glass ampoule, 0.25 g (2.1 mmol) of boron trichloride were condensed at liquid nitrogen temperature. The ampoule was sealed and kept at ambient temperature for 24 h. Thereafter, the ampoule was opened, the reaction mixture was transferred to a Schlenk flask, and the solvent was removed in vacuo. The solid obtained (2.2 g; 88% yield) was recrystallized from dichloromethane yielding 1.8 g of colourless crystals.

3b: C₂₄H₁₈BF₃₆O₉P₃ (1238.08); MS *m/e* 1238; Anal. Calcd.: C, 23.28; H, 1.46; F, 55.24; P, 7.50. Found: C, 23.53; H, 1.53; F, 55.00; P, 7.30%. ¹H NMR (CD₂Cl₂) δ 1.26, 2.73 (m); ³¹P NMR (CD₂Cl₂) δ 61.2; ¹⁹F NMR (CD₂Cl₂) δ –68.6, –70.0.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

References

- [1] R.G. Cavell, R.D. Leary, A.J. Tomlinson, *Inorg. Chem.* 11 (1972) 2578.

- [2] F. Ramirez, M. Nowakowski, J.F. Marecek, *J. Am. Chem. Soc.* 98 (1976) 4330.
- [3] M. Volkholz, O. Stelzer, R. Schmutzler, *Chem. Ber.* 111 (1978) 890.
- [4] D. Schomburg, N. Weferling, R. Schmutzler, *J. Chem. Soc., Chem. Commun.* 810 (1981).
- [5] M. Witt, K.S. Dhathathreyan, H.W. Roesky, *Adv. Inorg. Chem. Radiochem.* 30 (1986) 223.
- [6] W.S. Sheldrick, N. Weferling, R. Schmutzler, *Liebigs Ann. Chem.* 1035 (1981).
- [7] J. Powell, K.S. Ng, J.F. Sawyer, *Chem. Commun.* 1131 (1987).
- [8] R. Schmutzler, O. Stelzer, N. Weferling, *Chem. Ber.* 121 (1988) 391.
- [9] H.R. Allcock, R.L. Kugel, G.Y. Moore, *Inorg. Chem.* 14 (1975) 2831.
- [10] A.B. Burg, J.S. Basi, *J. Am. Chem. Soc.* 90 (1968) 3361.
- [11] A.B. Burg, J.S. Basi, *J. Am. Chem. Soc.* 91 (1969) 1937.
- [12] S. Berger, S. Braun, H.O. Kalinowski, *NMR-Spektroskopie von Nichtmetallen, ³¹P NMR-Spektroskopie*, Vol. 3, Georg Thieme Verlag, Stuttgart, New York, 1993.
- [13] D. Schomburg, O. Stelzer, N. Weferling, R. Schmutzler, W.S. Sheldrick, *Chem. Ber.* 113 (1980) 1566.