Acid Anhydrides

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Tetrakis[2,4-bis(trifluoromethyl)phenyl]diphosphoxane: An Anhydride of a Phosphinous Acid**

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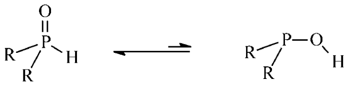
Diorganylphosphinous acids, R_2POH, are generally unstable with respect to their tautomeric counterparts $R_2P(O)H$ [Eq. (1)]. In 1960, Burg and Griffiths demonstrated that the unusual form of a phosphinous acid can be stabilized by the strongly electron-withdrawing trifluoromethyl group.[1]



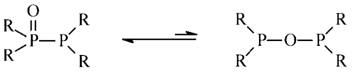
(1)

Bis(trifluoromethyl)phosphinous acid, $(CF_3)_2POH$, exists in the gas phase as a mixture of two rotational isomers, and it is to date the only example of a neutral phosphinous acid that is stable with respect to its tautomeric phosphane oxide structure.[2]

Very recently Cowley and co-workers succeeded in the stabilization of a phosphinous acid derivative as a β-diketiminato-supported hydroxyphosphenium cation.[3]

The claimed[4] bis(pentafluorophenyl)phosphinous acid, $(C_6F_5)_2POH$, has been shown to exist in the solid state as well as in $CHCl_3$, toluene, and CH_3CN exclusively as the phosphane oxide.[5] The phosphinous acid tautomer can only be observed in solvents with high donor numbers (e.g. DMF, THF).[5] Substituents with a stronger electron-withdrawing effect than the C_6F_5 group, for example, the *p*-tetrafluoropyridyl group,[6] effect a further stabilization of the phosphinous acid tautomer,[5] while the increased steric demand of a 2,4-bis(trifluoromethyl)phenyl group ($2,4-(CF_3)_2C_6H_3$) favors the phosphane oxide tautomers.[7]

The anhydrides of phosphinous acids, $R_2P-O-PR_2$, exhibit a similar behavior. In general, these compounds are less stable than the corresponding diphosphane monoxides, $R_2P(O)-PR_2$ [Eq. (2)].

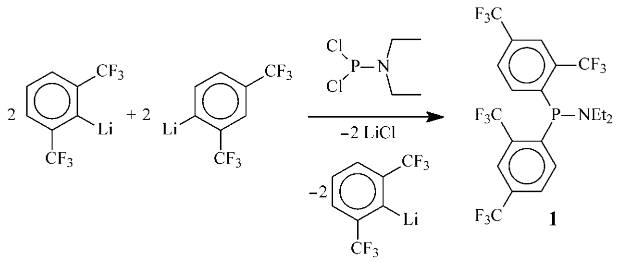


(2)

As known for phosphinous acids, the anhydride can also be stabilized by strongly electron-withdrawing substituents such as the CF_3 group.[1] Although tetrakis(trifluoromethyl)-diphosphoxane, $(CF_3)_2P-O-P(CF_3)_2$, and $(CF_3)_2POH$ are stable with respect to their corresponding phosphane oxide tautomers, the colorless liquids with high vapor pressure are highly reactive and immediately deflagrate on contact with air.

While sterically demanding groups destabilize the phosphinous acid form, anhydrides can be stabilized by bulky *t*Bu groups, as demonstrated in 1976 by Veits and co-workers.[8] On the basis of these results, the electron-withdrawing and sterically demanding 2,4-bis(trifluoromethyl)phenyl group is expected to be ideal for the stabilization of the unusual form of diphosphoxane derivatives, the anhydrides of phosphinous acids.

The reaction of 1,3-bis(trifluoromethyl)benzene with *n*-butyllithium gives a mixture of 2,6- and 2,4-bis(trifluoromethyl)phenyl lithium, (Scheme 1). Treatment of PCl_3 with an excess of the lithiated bis(trifluoromethyl)phenyl derivatives leads to the formation of a complex product mixture of differently substituted 2,6- and 2,4-bis(trifluoromethyl)phenylphosphanes.[9] To achieve a selective synthesis of bis[2,4-bis(trifluoromethyl)phenyl]phosphane derivatives, a bulky substituent has to be attached to the phosphorus center to avoid the attack of the more sterically demanding 2,6-bis(trifluoromethyl)phenyl moiety. According to this idea, we investigated the reaction of dichlorodiethylaminophosphane, Cl_2PNEt_2, with a mixture of 2,6- and 2,4-bis(trifluoromethyl)phenyl lithium, which allowed the selective synthesis of the aminophosphane derivative **1**.[10]



Scheme 1. Synthesis of bis[2,4-bis(trifluoromethyl)phenyl]diethylaminophosphane (**1**).

Upon treatment with concentrated hydrochloric acid, **1** is selectively converted into the corresponding chlorophosphane **2** (Scheme 2), which is hydrolyzed by aqueous THF to the phosphane oxide **3** (83 %). Compound **3** reacts with an

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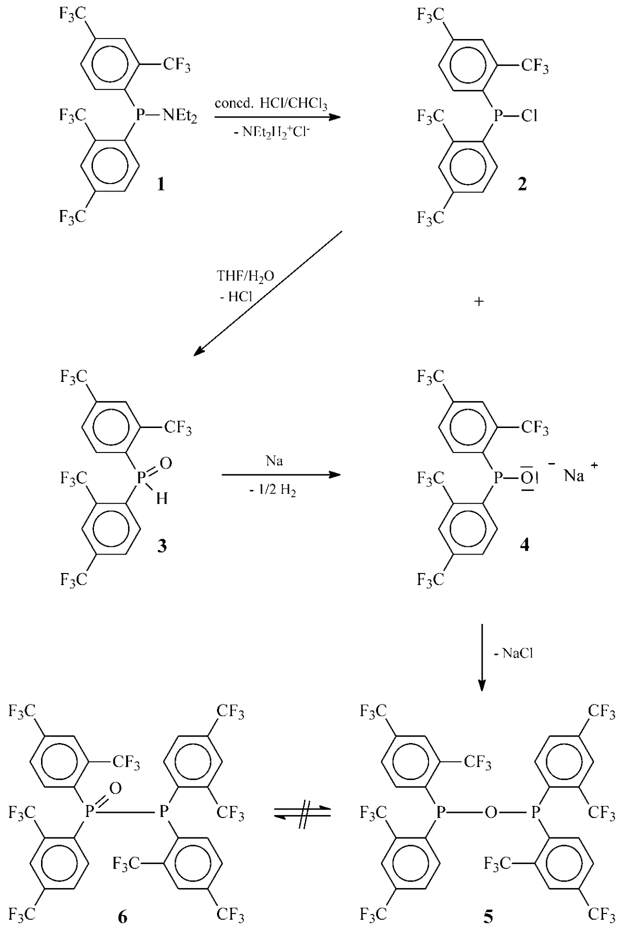

Scheme 2. Synthesis of tetrakis[2,4-bis(trifluoromethyl)phenyl]diphosphoxane (**5**).

excess of elemental sodium to the corresponding phosphinite salt **4**.[10]

Treatment of **4** with the chlorophosphane **2** allows the selective synthesis of the tetraorganyl diphosphoxane derivative **5** (Scheme 2). The isomeric diphosphane monoxide **6** is formed only as a minor product, which could be identified by its characteristic resonances in the ^{31}P NMR spectrum at $\delta = 39.0$ ppm for the oxygen-bonded phosphorus atom and at $\delta = -32.5$ ppm for the trivalent phosphorus atom. The doublet splitting of 247 Hz matches the expected range of $^{1}J_{\mathrm{P,P}}$ couplings. In the absence of acids, no rearrangement of the diphosphane monoxide **6** and diphosphoxane **5** has been observed.

The ^{19}F NMR spectrum of **5** in $CDCl_3$ exhibits two resonances, one singlet at $\delta = -63.3$ ppm for the CF_3 group in *para* position and one multiplet at $\delta = -57.1$ ppm for the CF_3 group in *ortho* position. The multiplet splitting is caused by the coupling to two magnetically non-equivalent phosphorus atoms. The ^{19}F and the ^{31}P NMR spectra (Figure 1) both show higher-order resonances of an $[AX_6]_2$ spin system ($A = {}^{31}$P and $X = {}^{19}$F) with $^{4}J_{\mathrm{P,F}}$ and $^{6}J_{\mathrm{P,F}}$ couplings of +60.8 and +5.4 Hz, respectively. Because the long-range F,F coupling of the *ortho* CF_3 groups along the P-O-P unit is close to zero, only the relative signs of the $^{4}J_{\mathrm{P,F}}$ and $^{6}J_{\mathrm{P,F}}$ couplings could be determined. After iteration of the ^{31}P and ^{19}F NMR resonances, the absolute value of the $^{2}J_{\mathrm{P,P}}$ coupling is calculated to be 172.3 Hz.

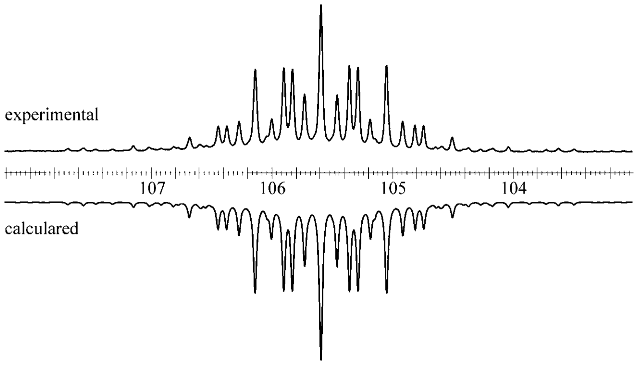

Figure 1. Experimental and calculated $^{31}P\{^{1}H\}$ NMR spectrum of **5**.

As expected, the diphosphoxane **5** is sensitive to hydrolysis. NMR spectroscopic investigations in $CDCl_3$ always allowed the detection of the phosphane oxide **3** as the product of hydrolysis. However, colorless crystals of the diphosphoxane **5** can be handled for short periods in ambient atmosphere without significant decomposition.

The diphosphoxane **5** crystallizes in the monoclinic space group *C*2/c (No. 15) with one molecule in the asymmetric unit. The molecular structure exhibits a twofold synperiplanar arrangement of the phosphorus lone pairs with respect to the opposite P–O bond, resulting in a molecular structure with approximate C_2 symmetry (Figure 2). The trifluoromethylated nitrogen derivative $(CF_3)_2N\text{-}O\text{-}N(CF_3)_3$ shows a comparable structural motif.[11] The P–O bond lengths of the diphosphoxane **5** (165.6(3) and 166.1(3) pm) are in the typical range of P–O single bonds. Bis(trifluoromethyl)phosphinous acid, $(CF_3)_2POH$, exhibits a comparable P–O separation of 166.1(4) pm in the gas phase.[2]

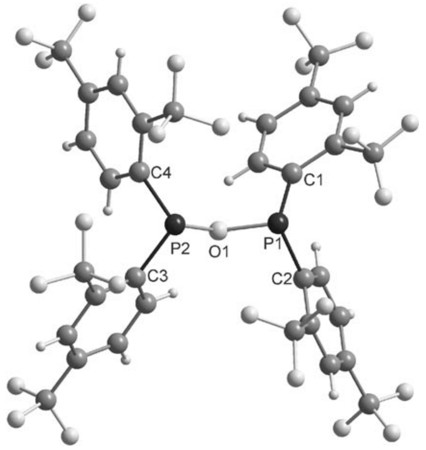

Figure 2. Molecular structure of diphosphoxane **5**. Selected bond lengths [pm] and angles [°]: P1-O1 165.6(3), P2-O1 166.1(4), P1-C1 185.3(3), P1-C2 186.7(4), P2-C3 184.8(4), P2-C4 187.1(4); P1-O1-P2 119.7 (2), C1-P1-C2 100.0(2), C3-P2-C4 99.4(2).

The strong electron withdrawal and high steric demand of the 2,4-$(CF_3)_2C_6H_3$ group are ideally suited to stabilize the unusual form of a diphosphoxane—the anhydride of a phosphinous acid. The higher steric demand of the 2,6-$(CF_3)_2C_6H_3$ group has, to date, prevented the selective synthesis of a diphosphoxane derivative bearing one 2,4- and one 2,6-$(CF_3)_2C_6H_3$ group at each phosphorus atom.

Experimental Section

5: Bis[2,4-bis(trifluoromethyl)phenyl]phosphane oxide (1.2 g, 2.6 mmol) in 1,2-dimethoxyethane (15 mL) is treated for two hours at room temperature with an excess of elemental sodium. After filtration under inert conditions, chlorobis[2,4-bis(trifluoromethyl)-phenyl]phosphane (1.1 g, 2.1 mmol) in diethyl ether (30 mL) is added to the light-orange solution. After stirring for three minutes at room temperature, hexane (200 mL) is added to complete the precipitation of inorganic salts. Subsequent filtration under inert conditions and removal of the solvents in vacuum yielded **5** (1.7 g, 1.8 mmol; 86 %). Single crystals were obtained on recrystallization from diethyl ether at −30 °C. Elemental analysis (%) calcd for **5**: C 41.31, H 1.30; found: C 41.14, H 1.35. MS (20 eV; $R = C_6H_3(CF_3)_2$): *m*/*z* (%): 930 (100) $[M^+]$, 911 (10) $[M^+{-}F]$, 861 (4) $[M^+{-}CF_3]$, 670 (26) $[PR_3^+]$, 473 (100) $[M^+{-}PR_2]$. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.4$–8.0 ppm (m). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 141.7$ (m, C1), 133.8 (m, C2), 123.8 (s, br, C3), 133.1 (q, $^2J_{F,C} = 33.9$ Hz, C4), 128.3 (q, $^3J_{F,C} = 3.5$ Hz, C5), 132.4 (s, br, C6), 123.0 (q, $^1J_{F,C} = 275.8$ Hz, C7), 122.8 ppm (q, $^1J_{F,C} = 272.8$ Hz, C8). ^{19}F NMR (188 MHz, $CDCl_3$, 25 °C, $CFCl_3$): $\delta = -63.3$ (s, 12 F), −57.1 ppm (m, X part of an $[AX_6]_2$ spin system with $A = {}^{31}P$). ^{31}P NMR (81 MHz, $CDCl_3$, 25 °C, H_3PO_4): $\delta = 105.6$ ppm (m, A part of an $[AX_6]_2$ spin system with $X = {}^{19}F$).

Data collection for X-ray structure determination was performed on a STOE IPDS II diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation (71.073 pm). The data were corrected for Lorentz and polarization effects. A numerical absorption correction based on crystal-shape optimization was applied for all data (*X-Shape 2.01, Crystal Optimisation for Numerical Absorption Correction*, STOE & Cie GmbH, Darmstadt, **2001**). The programs used herein are Stoe's X-Area (*X-Area 1.16*, Stoe & Cie GmbH Darmstadt, **2003**), including X-RED and X-Shape for data reduction and numerical absorption correction (*X-RED32 1.03, Stoe Data Reduction Program*, Stoe & Cie GmbH, Darmstadt, **2002**), and X-Step32 program (*X-STEP32 1.06f*, Stoe & Cie GmbH, Darmstadt, **2000**), including SHELXS-97 (G. M. Sheldrick, *SHELXS-97*, University of Göttingen, **1998**) and SHELXL-97 (G. M. Sheldrick, *SHELXL-97*, University of Göttingen, **1997**) for structure solution and refinement. All hydrogen atoms were placed in idealized positions using a riding model.

The last refinement cycles included atomic positions for all atoms, anisotropic thermal parameters for all non-hydrogen atoms, and isotropic thermal parameters for all hydrogen atoms. Intensity data for **5** ($C_{32}H_{12}F_{24}OP_2$; 930.36 g mol^{-1}): $T = 298$ K, colorless transparent plate, monoclinic, space group *C*2/c (No. 15), $a = 2468.7(1)$, $b = 934.5(6)$, $c = 3188.4(2)$ pm, $\beta = 94.897(5)°$, $V = 7.328$ nm^3, $Z = 8$, $\rho_{calcd} = 1.686$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.269$ cm^{-1}, $F(000) = 3664$; 45929 reflections with $3.12 < 2\theta < 54.2°$, 8000 independent reflections in structure solution and refinement for 532 parameters, R_1 $(I \geq 2\sigma(I)) = 0.078$, wR_2 (all data) $= 0.228$, $w = 1/\{\sigma^2(F_o^2) + [0.1666(F_o^2 + 2F_c^2)/3]^2\}$. CCDC-678308 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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