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Tetrakis(trimethysilyl)hypophosphate $P_2O_2(OTMS)_4$: Synthesis, Reactivity and Application as Flame Retardant

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ABSTRACT: *The preparation of tetrakis(trimethysilyl)hypophosphate, $P_2O_2(OTMS)_4$ ($TMS = SiMe_3$), which is easily obtained from cheap starting materials, is reported. Reaction with protic substrates (H_2O, alcohols) proceeds under stepwise cleavage of silylethers, ROTMS, and formation of hypophosphoric acid, $P_2O_2(OH)_4$. Amines in the presence of molecular sieves lead to desilylation and formation of ammonium salts of the $[P_2O_2(OTMS)_2(O^-)_2]$ dianion. On cotton fabrics, $P_2O_2(OTMS)_4$ hydrolyzes to give $P_2O_2(OH)_4$ within about 1 h when exposed to air, and this compound acts as an efficient flame retardant (limiting oxygen index >26%) even at low loadings (P content <3%).* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:721–731, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20373

INTRODUCTION

Hypophosphoric acid $(HO)_2OP\text{-}PO(OH)_2 = P_2O_2(OH)_4$ and its salts have frequently been used as dopant for conductive polymers [1], as acidic catalysts for polycondensations [2,3], as lubricants [4–6], and also as flame retardants [7,8]. In addition, hypophosphates were studied as ligands for the complexation of metals [9], and they were employed in biochemistry, where they were used as substitutes for phosphate groups [10].

Although inorganic hypophosphates are known for a long time, few organylhypophosphates $P_2O_2(OR)_4$ have been reported (Scheme 1). The first reaction leading to hypophosphoric acid was reported in 1859 [11], and the salt was characterized in 1877 by Salzer [12]. Since the 1960s, few studies were performed on hypophosphates, probably due to the limited accessibility of these types of compounds; whereas for the preparation of diphosphane oxides $R_2(O)P\text{-}P(O)R_2$, various methods are known [13,14], only two different reactions are reported to access either hypophosphoric acid [15,16] or tetraalkylhypophosphates [17,18]. The only derivatives reported so far are disodium and diammonium salts of dialkyl hypophosphates, obtained by dealkylation of tetraalkylhypophosphates [19]. X-ray diffraction studies revealed the structures of several

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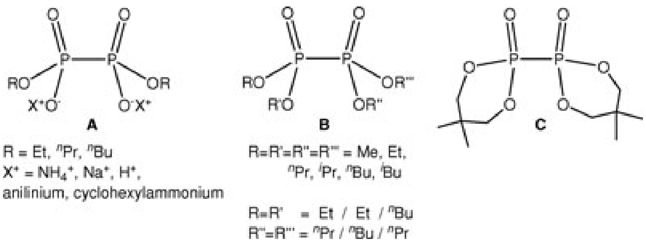


SCHEME 1 Summary of the published alkyl-substituted hypophosphate molecules.

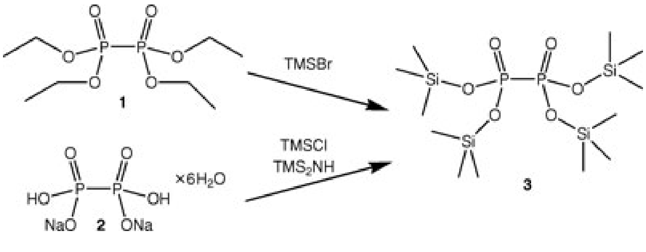
inorganic salts of hypophosphoric acid and of **C** as the only alkyl-substituted organohypophosphate [20].

We became interested in organohypophosphates as potential flame retardants as part of an ongoing program established in our laboratory [21–23]. We report here two synthetic routes to obtain the previously unknown persilylated tetrakis(trimethysilyl)hypophosphate. We investigated parts of the chemical reactivity of the title compound and its ability to act as a flame retardant.

RESULTS AND DISCUSSION

The starting materials $P_2O_2(OEt)_4$ **1** and $P_2O_2(OH)_2(ONa)_2 \times 6H_2O$ **2** were obtained according to the published procedures [15–17]. For the synthesis of tetrakis(trimethysilyl)hypophosphate $P_2O_2(OTMS)_4$ **3** (TMS = $SiMe_3$), two different preparations were developed (Scheme 2). In the first procedure, trimethylsilylbromide was added dropwise to a dichloromethane solution of **1** at 0°C in analogy to the silylation of phosphonic acid dialkyl esters [24]. Initially, a mixture of compounds was observed in the ^{31}P NMR spectrum, which we assigned to be the mono-, bis-, and tris-TMS-substituted hypophosphate (see Table 1 for ^{31}P NMR data). The assignment of the resonances to the compounds listed in Table 1 was made by inspection of the evolution of the relative signal intensities with time and the observed spin systems.

Although the symmetrically substituted species show a singlet resonance, asymmetrically substituted ones show AB spin systems with a strong roof effect due to large P—P couplings ($^1J_{PP} > 700$ Hz) [25]. The successive substitution of the ethyl groups by TMS provokes a shift to lower frequencies from $\delta = +6.5$ ppm in $P_2O_2(OEt)_4$ **1** to $\delta = -10.3$ ppm in $P_2O_2(OTMS)_4$ **3**. Note that of the seven possible compounds [**1**, $(EtO)_2OP\text{-}PO(OEt)(OTMS)$, *rac*-(EtO)(TMSO)OP-PO(OTMS)(OEt), *meso*-(EtO)(TMSO)OP-PO(OTMS)(OEt), $(EtO)_2OP\text{-}PO(OTMS)_2$, (EtO)(TMSO)OP-$PO(OTMS)_2$, **3**], only five are actually observed in the reaction mixture (under the assumption that all species show different NMR resonances). The asymmetrical $(EtO)_2OP\text{-}PO(OTMS)_2$ can be excluded, and we assume that the pairs of enantiomers *rac*-(EtO)(TMSO)OP-PO(OTMS)(OEt) are not formed for steric reasons. After 12 h at room temperature, the formation of $P_2O_2(OTMS)_4$ **3** was complete (conversion >98%), judged upon the ^{31}P and ^1H NMR spectra. Compound **3** was isolated by simply removing the volatile materials under high vacuum leaving a waxy solid.



SCHEME 2 Two reaction pathways yielding tetrakis(trimethylsilyl)hypophosphate.

TABLE 1 ^{31}P NMR Shifts of the Intermediates Observed During the Reaction of Tetraethylhypophosphate **1** with TMSBr, Measured in CD_2Cl_2

Molecule	*δP (ppm)*	*δP (ppm)*	*$^1J_{PP}$ (Hz)*
$P_2O_2(OEt)_4$	6.5		
$P_2O_2(OEt)_3(OTMS)$	−3.2	7.2	751
meso-$P_2O_2(OEt)_2(OTMS)_2$	−1.9	–	–
$P_2O_2(OEt)(OTMS)_3$	−11.3	−1.0	815
$P_2O_2(OTMS)_4$	−10.3	–	–

In the second procedure, a suspension of $P_2O_2(OH)_2(ONa)_2 \times 6H_2O$ **2**, hexamethyldisilazane and trimethylsilylchloride in dichloromethane was refluxed for 12 h. The reaction was slow due to the very low solubility of **2** in organic solvents. In contrast to the reaction of **1** with TMSBr, no intermediates were observed in the ^{31}P NMR spectra in the course of the reaction. After removing the remaining starting material and NaCl by filtration and hexamethyldisiloxane by evaporation, about 80% yield of **3** was isolated. Because of the readily available starting materials, this synthesis is a convenient procedure.

Alcoholysis of **3**

To a solution of **3** in dichloromethane, an excess of ethanol (ca. 16 eq.) was added. Analysis of the reaction mixture after 15 min by ^1H, ^{31}P, and ^{29}Si NMR spectroscopy revealed that ethyl groups had replaced about 50% of the TMS groups forming EtOTMS and a mixture of silylated hypophosphates $P_2O_2(OTMS)_x(OH)_{4-x}$ ($x = 0$–3; see Table 2 for ^{31}P NMR data and assignments).

TABLE 2 ^{31}P NMR Shifts of the Intermediates Observed During Alcoholysis of **3**, Measured in CD_2Cl_2

Molecule	*δP (ppm)*	*δP (ppm)*	*$^1J_{PP}$ (Hz)*
$P_2O_2(OTMS)_3(OH)_1$	−9.7	−2.7	826
$P_2O_2(OTMS)_2(OH)_2$	−1.6	–	–
$P_2O_2(OTMS)_1(OH)_3$	−1.2	5.3	748
$P_2O_2(OH)_4$	5.9	–	–

The hypophosphate mixture consisted mainly of $P_2O_2(OTMS)_3(OH)$, $P_2O_2(OTMS)_2(OH)_2$, and $P_2O_2(OTMS)(OH)_3$; however, **3** ($x = 4$) and hypophosphoric acid ($x = 0$) were also present in minor amounts. The composition of the mixture did not change significantly with time and even with a large excess of ethanol, the conversion reached only 50%. Addition of a large excess of EtOTMS led to the reformation of **3** as the main product and some $P_2O_2(OTMS)_3(OH)$. However, upon evaporation of the volatiles, hypophosphoric acid $P_2O_2(OH)_4$ formed quantitatively. Clearly, a thermodynamic equilibrium exists in solution between all species $P_2O_2(OTMS)_x(OH)_{4-x}$ listed in Table 2 and only removal of the volatile materials shifted the equilibrium to the product side. Similar equilibria were observed with different alcohols, for example, allylalcohol, ethylene glycol or $HOCH_2CH_2OCOCHCH_2$. All reactions showed mixtures of products.

Hydrolysis of 3

3 was hydrolyzed by dissolving it in THF and slowly adding a H_2O/THF mixture. During the addition, the same intermediates as in the alcoholyses were identified by NMR spectroscopy. Adding an excess of water caused clean and rapid hydrolysis of **3** to hypophosphoric acid.

Reaction of 3 *with Amines*

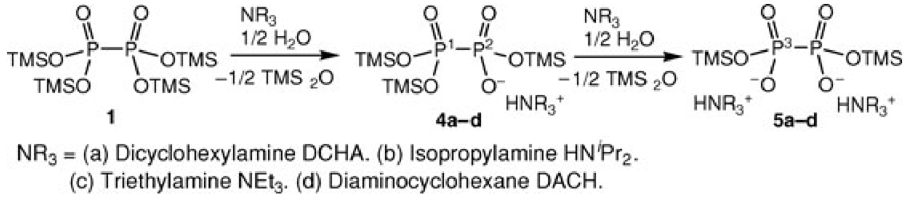
Several authors reported that ammonium salts of phosphonates were obtained from silylated phosphonates either upon hydrolysis with water or alcohols and subsequent dissolution in amines [27,28] or by hydrolysis in the presence of amines [29]. The second method was successfully applied in cases where the formed phosphorus acid was unstable.

The behavior of **3** upon desilylation in the presence of amines was investigated; the reactions are summarized in Scheme 3. First, the reaction of dicyclohexylamine (DCHA) with **3** was studied. A solution of DCHA and **3** in dichloromethane in the presence of molecular sieves (4 Å) was stirred at 40°C. The reaction was monitored by ^{31}P and ^{29}Si NMR spectroscopy. Curiously, without molecular sieves the reaction took several days (only 10% conversion after one day at 40°C).

In the presence of molecular sieves, upon addition of 1 equivalent of DCHA, the singly desilylated hypophosphate **4a** formed after 6 h. The water required for this reaction to take place is present in the solvent, which was not dried prior to the reaction. **4a** was identified by NMR spectroscopy, and it was stable for one day at room temperature in solution in the absence of molecular sieves. Attempts to isolate the product by evaporation of the volatile materials yielded an unidentified product with a broad ^{31}P NMR signal at −1.8 ppm.

When 2 equivalents or even an excess of DCHA was reacted with **3**, within 12 h the insoluble salt bis(dicyclohexylammonium)-bis-(trimethylsilyl)hypophosphate $[P_2O_2(OTMS)_2(O^-)_2] \times 2\ H\mathit{DCHA}^+$ **5a** precipitated. The salt was isolated by filtration and was stable in argon atmosphere at room temperature for months. **5a** was insoluble in THF, DMSO, hexane, toluene, chlorobenzene, ether, and only poorly soluble in dichloromethane. It decomposed upon heating for 1 h at 80°C in DMSO.

The obtained products showed characteristic ^{31}P NMR shifts that are summarized in Table 3. Upon desilylation, the phosphorus resonance moved to higher frequencies. **4a** showed two doublets at −7.2 ppm and at 0.4 ppm with $^1J_{PP}$ = 748 Hz, whereas **5a** showed a singlet at 4.2 ppm. The ^{29}Si chemical shifts of the TMS groups of the hypophosphates moved to lower frequencies upon desilylation. The tetrasilylated hypophosphate showed a singlet at 24.3 ppm, and the singly desilylated



SCHEME 3 Desilylation in the presence of amines yields the bis-silylated hypophosphate dianions **5a–d** as the final products.

TABLE 3 Collected ^{31}P NMR Data of the Tris-Silylated and Bis-Silylated Hypophosphate Salts [(TMSO)$_2$OP^1-P^{2}O(OTMS)(O$^-$)] Cat$^+$and [P$^3_2$(O)$_2$(OTMS)$_2$(O$^-$)$_2$] (Cat$^+$)$_2$ in CD$_2$Cl$_2$

Cation	δP^1 *(ppm)*	δP^2 *(ppm)*	$^1J_{PP}$ *(Hz)*	δP^3 *(ppm)*
H*DCHA*$^+$	−7.2	0.4	748	4.2
$H_2N(^iPr)_2^+$	−7.5	0.0	755	2.3
$HNEt_3^+$	−5.0	0.6	740	3.3
H*DACH*$^+$	−5.8	0.2	740	3.3

hypophosphate **4a** showed two signals at 19.7 and at 15.3 ppm. The chemical shift of **5a** was found at the lowest frequency, 12.5 ppm. The composition of **5a** is indicated by the integrated signal intensities of the protons belonging to the DCHA molecule and the TMS groups in the ^{1}H NMR spectrum.

Analogous reactions were observed with other amines. For example, the reaction of diisopropylamine with **3** was very slow in the absence of molecular sieves. But in the presence of molecular sieves, 1 equivalent of diisopropylamine reacted with **3** to give the singly desilylated product **4b** after 1 hour at 40°C. Upon addition of 2 equivalents of diisopropylamine, the soluble product **5b** was formed within 8 h (the NMR data are summarized in Table 3). Further heating led to degradation of the products. Also when 2 equivalents of the tertiary amine triethylamine, NEt_3, were added, the singly desilylated product **4c** was observed as intermediate, which then reacted to the bis-desilylated product **5c**.

Unlike the reactions with the amines DCHA and HN^iPr_2, the reaction of 1 equivalent of (*S,S*)-1,2-diaminocyclohexane (DACH) with **3** in chloroform in the presence of molecular sieves produced a mixture of **4d, 3**, and **5d**. However, upon addition of 2 equivalents of DACH, **5d** was obtained in pure form. Slow evaporation of the solvent gave crystals suitable for an X-ray structural analysis. It is noteworthy that the di-amine DACH was not protonated twice and the formula of **5d** reads [P$_2$O$_2$(OTMS)$_2$(O$^-$)$_2$] × 2 H*DACH*$^+$.

Reactions of the Desilylated Products

Regitz and Martin [30] reported the reaction of ammonium methyl α-diazaphosphonates with acetyl chloride giving the mixed anhydrides. In a related reaction, **5d** was reacted with acryloyl chloride in dichloromethane which led to a precipitate that we were unable to characterize. The tetrasilylated hypophosphate **3** was the only phosphorus-containing product in solution.

*Alcoholysis of [P$_2$O$_2$(OTMS)$_2$(O$^-$)$_2$] × 2 H*DCHA*$^+$ **5a***

5a, insoluble in common aprotic organic solvents and only poorly soluble in CH$_2$Cl$_2$, was soluble in a dichloromethane/ethanol mixture or in pure ethanol. **5a** was slowly solvolyzed in ethanol (90% after 3 days at room temperature) yielding EtOTMS, the salt [P$_2$O$_2$(OTMS)(OH)(O$^-$)$_2$] × 2 H*DCHA*$^+$, and the diammonium salt of the hypophosphate **2** [P$_2$O$_2$(OH)$_2$(O$^-$)$_2$] × 2 H*DCHA*$^+$ (identified by NMR spectroscopy).

Crystal Structure of **5d**

Crystals of the compound [P$_2$O$_2$(OTMS)$_2$(O$^-$)$_2$] × 2 H*DACH*$^+$ **5d** suitable for X-ray structural analysis were grown by slow evaporation of a chloroform solution. The salt crystallized in the monoclinic space group *C*2 with 8 molecules of hypophosphate, 16 molecules of H*DACH*$^+$, and about 26 molecules of chloroform per unit cell (shown in Fig. 1). One isolated hypophosphate dianion is shown in Fig. 2. Selected bond lengths are summarized in Table 4, details concerning the data collection and refinement can be found in Table 5 in the experimental section.

The hypophosphate dianions arrange in pairs with the eight oxygen atoms facing each other (and the TMS groups pointing away). The pair of anions is bridged by four H*DACH*$^+$ molecules, forming a

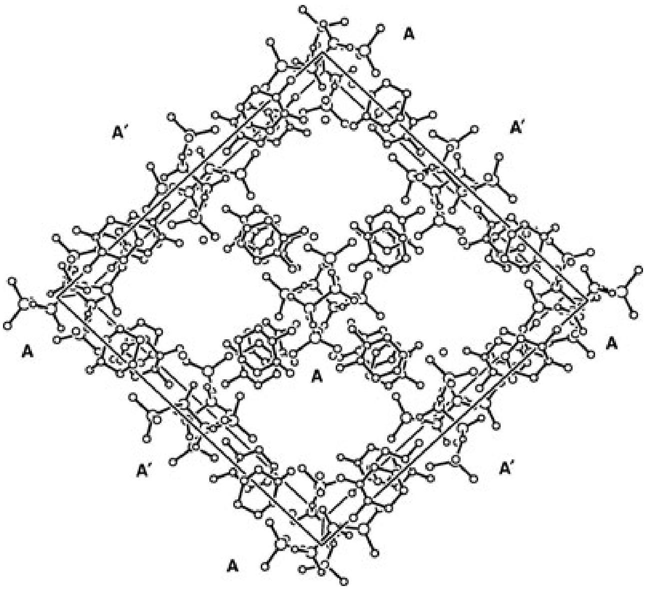


FIGURE 1 Pluto illustration of the structure of **5d**. The ellipsoid probability was set to 30%. View along the *b* axis. The chloroform molecules in the cavities are omitted for clarity

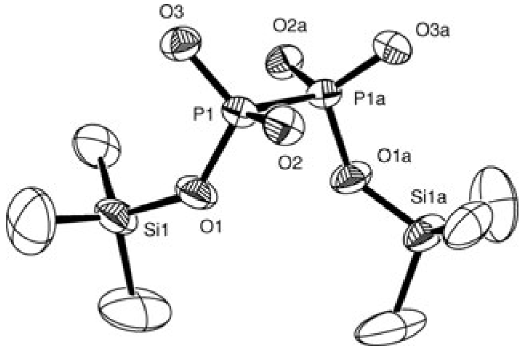


FIGURE 2 One hypophosphate unit of **5d**. The thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): P1–P1a: 2.203(2), P1–O1(Si): 1.588(3), P1–O2: 1.484(4), and P1–O3: 1.515(4).

TABLE 5 Crystallographic Data

$2\{[P_2O_4(OTMS)_2][C_6H_{10}(NH_2)(NH_3)]_2\} \times$·ca. $6.5CHCl_3$	
Empirical formula	$C_{42.43}H_{102.43}Cl_{19.29}N_8O_{12}P_4Si_4$
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$C2$
Unit cell dimensions	$a = 23.9240(18)$ Å $\alpha = 90°$ $b = 16.3271(12)$ Å $\beta = 94.0810(10)°$ $c = 24.0191(18)$ Å $\gamma = 90°$
Volume	9358.3(12) Å^3
Z	4
Density (calculated)	1.304 g/cm^3
Absorption coefficient	0.729 mm^{-1}
F(000)	3812
Crystal size	0.99 × 0.92 × 0.38 mm
Theta range for data collection	1.51° to 24.71°
Index range	$-18 \leq h \leq 27$, $-19 \leq k \leq 19$, $-28 \leq l \leq 27$
Reflections collected	18,902
Independent reflections	12756 [R(int) = 0.0178]
Absorption correction	Empirical (SADABS)
Data/restraints/parameters	12756/31/896
Flack parameter	$x = 0.04(7)$
Goodness-of-fit on F^2	1.041
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0584$, $wR_2 = 0.1651$
R indices (all data)	$R_1 = 0.0648$, $wR_2 = 0.1719$
Largest diff. peak and hole	0.702 and −0.440 e/Å^3

hexameric hydrogen-bridged aggregate (Fig. 3). The anionic and cationic species form a well-defined framework with rather wide cavities. These are filled with chloroform molecules. Four of these could be refined as a whole, whereas three other $CHCl_3$ molecules were disordered and had to be refined with free occupation variables (two of them were split into two independent positions). These poorly ordered solvent molecules only allowed for the wR_2 figure of merit to be refined to 17%. Nevertheless, the standard deviations of the bond lengths and angles of the molecules that form the actual salt compound are satisfactory.

The P—P bond distances range from 2.183(3) to 2.207(3) Å and are comparable with other hypophosphate anions and the alkyl substituted hypophosphate **C** (Scheme 1): $(NH_4)_2H_2P_2O_6$ [2.170(3) Å] [31], $Na_2H_2P_2O_6 \times 6H_2O$ [2.190(2) Å] [32], $Ni_2P_2O_6 \times 12H_2O$ [2.170(1) Å] [33], and **C** [2.20 Å] [20]. The P–O(Si) distances (1.58 ± 0.01 Å) are comparable to the P–O(H) distance in $(NH_4)_2H_2P_2O_6$ [1.572(5) Å]. The almost identical terminal P–O distances (1.50 ± 0.02 Å) are considerably shorter than the P–O(Si) distances and are in the typical range for phosphates [31].

Each H*DACH*$^+$ molecule is a singly protonated cation. The C–NH_3^+ distances (1.48 ± 0.01 Å) are slightly longer than the C–NH_2 distances (1.43 ± 0.03 Å). The ammonium groups point toward the P–O groups forming hydrogen bonds. The amine groups are oriented toward the outside of the aggregate. The N–O distances (2.71–2.83 Å) along the hydrogen bonds are on average somewhat shorter than the N–O distances observed for $(NH_4)_2H_2P_2O_6$ (average 2.93 Å). Each ammonium group forms three hydrogen bonds, whereas the oxygen atoms form either one or two hydrogen bonds as shown in Fig. 3.

TABLE 4 Selected Bond Lengths and Hydrogen Bonds (Å) for **5d**

	Bond Lengths		
P1–P1a	2.203(2)	P1–O1(Si)	1.588(3)
P2–P2a	2.207(3)	P2–O4(Si)	1.579(3)
P3–P3a	2.183(3)	P3–O7(Si)	1.581(3)
P4–P4a	2.194(2)	P4–O10(Si)	1.577(3)
P1–O2	1.484(4)	P1–O3	1.515(4)
P2–O6	1.489(3)	P2–O5	1.514(3)
P3–O9	1.499(4)	P3–O8	1.506(3)
P4–O11	1.482(4)	P4–O12	1.516(4)
N1–C13	1.479(6)	N2–C14	1.44(1)
N3–C19	1.489(8)	N4–C20	1.453(9)
N5–C25	1.482(7)	N6–C26	1.41(1)
N7–C31	1.471(6)	N8–C32	1.45(1)
	Hydrogen Bonds		
N1···O3	2.75(1)	N3···O2a	2.79(1)
N1···O8	2.83(1)	N3···O3	2.75(1)
N1···O9a	2.71(1)	N3···O8a	2.73(1)
N5···O5	2.76(1)	N7···O5a	2.76(1)
N5···O11	2.73(1)	N7···O6	2.77(1)
N5·O12a	2.78(1)	N7·O12a	2.73(1)

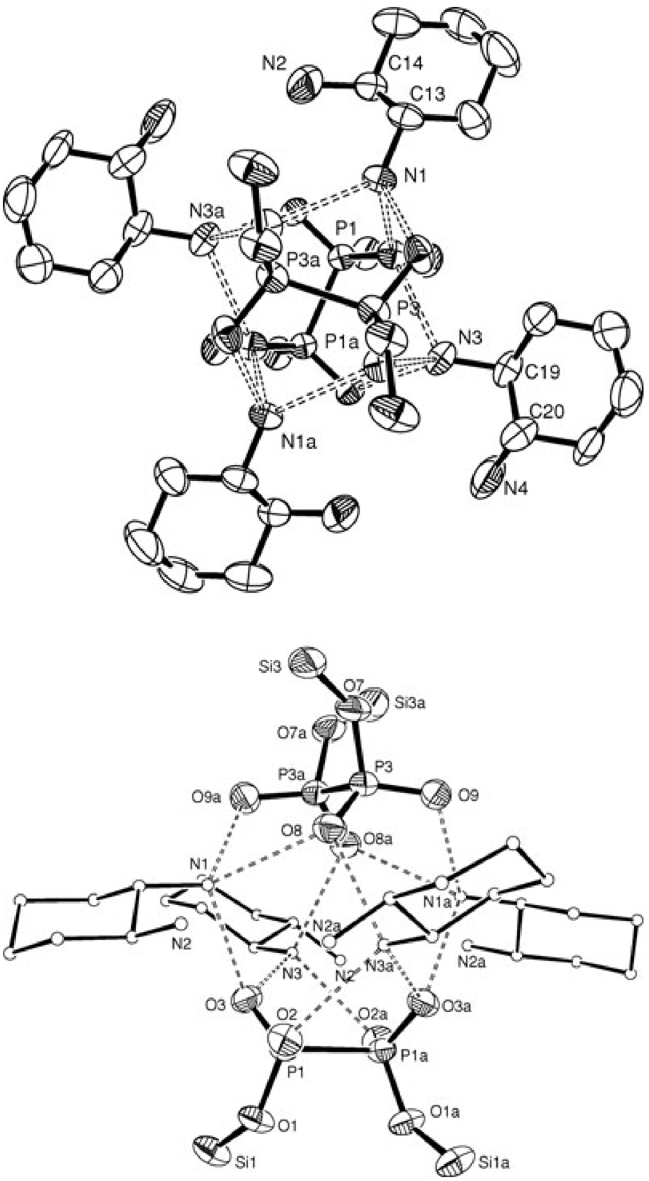


FIGURE 3 Section of the structure of **5d**: One hexameric aggregate containing two hypophosphate anions and four H*DACH*$^+$ cations. The hydrogen bonds are indicated with dashed lines. The methyl groups of the TMS substituents are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): N1···O3: 2.75(1), N1···O8: 2.83(1), N1···O9a: 2.71(1), N3···O2a: 2.79(1), N3···O3: 2.75(1), and N3···O8a: 2.73(1).

Flame Retardant Effect of Hypophosphates on Cotton Fabrics

Of all hypophosphates, only hypophosphoric acid $P_2O_2(OH)_4$ has been mentioned once in a patent as a potential flame retardant for synthetic thermosettable resins [7]. We were interested in investigating whether derivatives of hypophosphoric acid may serve as flame retardants for cotton fabrics. Here, we report briefly the first results of that study.

We chose $P_2O_2(OTMS)_4$ as potential flame retardant for our investigation and placed this onto cotton. Subsequently, the properties of these treated textile samples upon exposure to air and the resulting limiting oxygen index (LOI) were studied.

Flame Retardancy of $P_2O_2(OTMS)_4$-Treated Cotton Fabrics

Cotton samples were dried in high vacuum and then impregnated with a solution of $P_2O_2(OTMS)_4$ in dry diethylether. After evaporation of the solvent under reduced pressure, the dry samples were exposed to air and weighed. The weight increase (% loading) and the LOI were measured immediately after exposure to air and after 2 h at room temperature in contact with air. The values are summarized in Table 6.

The following observations were made: Despite a rather high loading with $P_2O_2(OTMS)_4$ (35.6%), a low LOI (21%) was measured when the sample was only briefly exposed to air (entry 1). Interestingly, a high LOI value (40%) was obtained when a sample with a comparably high-initial loading of $P_2O_2(OTMS)_4$ was exposed to air for about 2 h before the measurement (entry 2). As can be seen from entries 3 and 4, decreasing the loading to 19% and 8% still gave rise to very respectable LOI values (37% and 27%, respectively) after 2 h exposure of the vacuum-dried samples to air. Note in this context that fabrics with LOIs higher than 26% are considered to be flame retarded. Furthermore, generally 3% by weight of phosphorus is required on a fabric to obtain good flame retardancy. This is achieved when about 22% of $P_2O_2(OTMS)_4$ is loaded on the fabric whereby LOI >37% is reached. In other words, with only 8% loading (that is about 1% of P) a technically acceptable LOI can be obtained. The last entry of Table 6 shows that the hypophosphoric ethylester $P_2O_2(OEt)_4$ is

TABLE 6 Loading and LOI Measured for Flame-Retarded Cotton Samples

Flame Retardant	*Exposure Time to Air*	*% Loading*	*LOI (%O_2)*
$P_2O_2(OTMS)_4$	1 min	35.6	21
$P_2O_2(OTMS)_4$	2 h	30.7	40.5[a]
$P_2O_2(OTMS)_4$	2 h	18.9	37[a]
$P_2O_2(OTMS)_4$	2 h	7.8	27[a]
$P_2O_2(OEt)_4$		17.1	27

[a] The loading and the LOI were measured after 2 h. The active species is assumed to be $P_2O_2(OH)_4$.

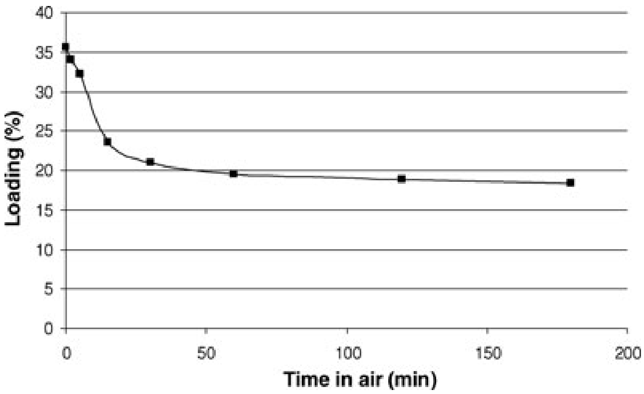


FIGURE 4 Decrease in the amount of loading of a $P_2O_2(OTMS)_4$-treated cotton sample after exposition to air.

significantly less efficient (LOI 27% reached with 17% loading corresponding to 3.7% P).

The observation that much better LOIs are obtained when $P_2O_2(OTMS)_4$- treated samples are exposed to air for about 2 h indicates a chemical change. In order to gain some insight into this process, we followed the fate of the cotton samples by weighing measurements, NMR, and IR spectroscopy as a function of the exposure time.

Weighing Measurements. The weight of treated cotton samples was stable in an inert atmosphere. Weighing measurements showed that upon exposure to air, the percentage of flame retardant added to the sample decreased within about 1 h to about half of the amount. After 1 h, the weight remained practically stable (Fig. 4).

Analysis with IR and NMR Spectroscopy. We assumed that the initial massive weight loss was due to the hydrolysis of the starting material leading to a volatile product. To confirm this hypothesis, the cotton samples were, at different times after exposition to air, analyzed with IR spectroscopy and extracted with dry dichloromethane or water. The washing solutions were analyzed by ^{1}H, ^{31}P, and ^{29}Si NMR spectroscopy.

The IR spectra of the cotton samples treated with $P_2O_2(OTMS)_4$ were compared to the spectrum of pure $P_2O_2(OTMS)_4$ (Fig. 5). The following bands were attributed to the TMS groups of $P_2O_2(OTMS)_4$ by comparison with the IR spectrum of hexamethyldisiloxane, TMS-O-TMS (HMDSO) [34]: ν (cm^{-1}) 2965/2905 (C—H stretch), 1242 (symmetric deformation of CH_3 groups), 829/762 (Si-C stretch).

The bands of $P_2O_2(OTMS)_4$ on cotton were clearly visible in the sample after 1 min in air. With increasing exposure time to air, the intensity of the TMS bands decreased and finally vanished after about 40 min. Note that after 40 min of exposure to air, the IR spectrum of the treated sample was similar to the one of untreated cotton. Weight measurements indicated, however, that 20% (m/m) of the initially added product remained. This is explained by the assumption that phosphate-like compounds form, for which the absorption bands overlap with those of cotton. Further information came from the NMR spectroscopic analysis of the dichloromethane extract. Five minutes after contact with air, already 50% of the TMS groups had been cleaved. As product HMDSO was identified (^{1}H, ^{29}Si NMR), besides, in the ^{31}P NMR spectrum, a mixture of the tris-silylated, bis-silylated, monosilylated hypophosphate, and hypophosphoric acid was identified. After 15 min, no ^{31}P NMR signal could be detected in the dichloromethane washing solution; small amounts of HMDSO were detected by ^{1}H

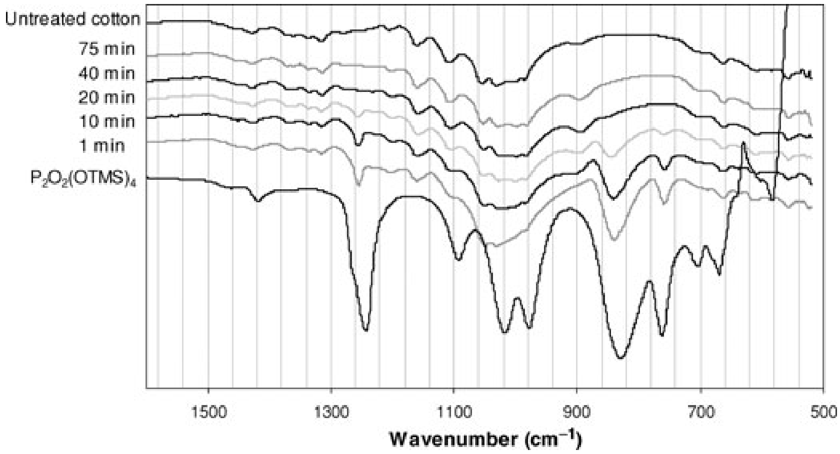


FIGURE 5 IR transition spectra of treated cotton samples with $P_2O_2(OTMS)_4$ after different times in air and comparison with $P_2O_2(OTMS)_4$ and virgin cotton.

NMR. The same results were obtained after 30 min. The weighing measurements showed that the weight of the sample was the same before and after washing. In a similar set of experiments with water as washing solvent, after 15 min exposition to air, a considerable amount of HDMSO molecules was detected by ^1H NMR spectroscopy. After 1 h, no HDMSO was detected. In the ^{31}P NMR spectrum, hypophosphoric acid was identified in the presence of traces of phosphoric and phosphorous acid.

We conclude that upon exposure of cotton treated with $P_2O_2(OTMS)_4$ to air, the TMS groups are quantitatively cleaved by hydrolysis within 1 hour. The insolubility of the final product in dichloromethane indicates the formation of a highly polar product, which is hypophosphoric acid, $P_2O_2(OH)_4$. These observations are fully consistent with the reactivity studies in solution with alcohols, ROH, which also proceed under formation of $P_2O_2(OH)_4$. The presence of HMDSO in the cotton sample after short contact with air explains the unexpected high flammability (LOI only 21%). HMDSO is a flammable liquid with a moderately low-boiling point (101°C/760 mmHg). It evaporates during longer exposure times (see weight loss) leading to an increase in the LOI.

CONCLUSION

A simple method for the synthesis of the tetrasilylester $P_2O_2(OTMS)_4$ could be developed using cheap starting materials. With protic substrates (H_2O, alcohols), this compound undergoes solvolysis to hypophosphoric acid, $P_2O_2(OH)_4$, and the corresponding silylether. It is noteworthy that in solution an equilibrium between all possible species $P_2O_2(OTMS)_x(OH)_{4-x}$ ($x = 0$–4) exists. With amines, desilylation can be achieved in the presence of molecular sieves and the ammonium salts bis(dicyclohexylammonium)-bis-(trimethylsilyl)hypophosphate, $[P_2O_2(OTMS)_2(O^-)_2] \times 2\,H\mathit{DCHA}^+$ **5a**, and (*S*)-1-ammonium-(*S*)-2-aminocyclohexane-bis(trimethylsilyl)hypophosphate, $[P_2O_2(OTMS)_2(O^-)_2] \times 2\,H\mathit{DACH}^+$**5d** were obtained as colorless solids. Unfortunately, attempts to obtain hypophosphate derivatives, $P_2O_2(OTMS)_x(OR)_{4-x}$ with polymerizable R groups have failed so far. First experiments with $P_2O_2(OTMS)_4$, which gives $P_2O_2(OH)_4$ on air, as the active component showed that hypophosphates are in principle a very promising new class of flame retardants for cotton fabrics. However, $P_2O_2(OH)_4$ is only linked via hydrogen bonds to the cotton fabrics and not as initially intended via covalent phosphorus ester bonds formed in the reaction of $P_2O_2(OTMS)_4$ with cellulose hydroxyl functions. Consequently, the rather weakly bound hypophosphoric acid is easily removed upon washing with water. It will be the aim of further studies to prepare hypophosphates that allow a permanent grafting and sustainable flame retardancy of cotton fabrics.

EXPERIMENTAL

General Techniques

Where indicated, the syntheses were performed under an atmosphere of argon using standard Schlenk techniques. Dichloromethane was freshly distilled from calcium hydride. Air sensitive compounds were stored and weighed in an argon-filled glove box (Braun MB 150 B-G system). Molecular sieves were dried under high vacuum at about 200°C for 12 h until the vapor pressure remained constantly low.

NMR spectra were recorded on Bruker Avance 400, 300, 250 spectrometers. The chemical shifts (δ) are referenced according to IUPAC [35] and expressed in ppm relative to TMS, H_3PO_4 for ^1H, ^{13}C, ^{29}Si, and ^{31}P, respectively. Coupling constants J are given in hertz as absolute values. Where a first-order analysis is appropriate, the multiplicity of the signals is indicated as s, d, t, q for singlets, doublets, triplets or quadruplets, respectively. The abbreviation br is given for broadened signals.

IR spectra were measured on a Perkin-Elmer 2000 FT-IR spectrometer using a KBr beamsplitter.

Mass spectra were taken on a Finnigan MAT SSQ 7000 in the EI (70 eV) mode.

X-ray crystallographic measurements were performed on a Bruker SMART 1K platform with CCD area detector. Refinement was done with SHELXL-97 [36]. CCDC 613012 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Preparation of the Cotton Samples. Pieces (52 × 140 mm) of bleached, woven cotton fabrics (120 g/m^2) were weighed and immersed at room temperature for 1 min in a dichloromethane solution containing 140 g/L of **1** or **3** in ether. The impregnated fabrics were dried in vacuo.

Weighing Measurements. These measurements were used to monitor the amount of loading. The degree of loading and the percentage of phosphorus on the samples were determined as follows:

$$\text{Degree of loading (\% w/w)} = \frac{W_1 - W_0}{W_0} \times 100$$

$$\text{\% Phosphorus on sample (\% w/w)} = \frac{W_1 - W_0}{W_1} \times \%P_{\text{mol}} \times 100$$

where W_0 and W_1 are the weights of the cotton fabric samples before and after loading, respectively and $\%P_{\text{mol}}$ is the percentage of phosphorus in the molecule.

LOI Measurements. The flame retardancy of the untreated and treated fabrics was assessed by the LOI method, according to ISO 4589-2 using an oxygen index test apparatus from Fire Instrumentation Research Equipment Ltd. with a digital readout of the oxygen concentration to ±0.1%. The LOI value corresponds to the minimum concentration of oxygen in the mixture of oxygen/nitrogen necessary to burn the sample. The LOI values are given with a precision of ±0.5%.

Synthesis of Tetrakis(trimethysilyl)hypophosphate **3**

Reaction from Tetraethylhypophosphate **1**. Trimethylsilyl bromide (25 g, 0.16 mol) was added dropwise over 30 min to a solution of freshly distilled tetraethyl hypophosphate (9.0 g, 0.033 mol) in dry dichloromethane (50 mL) at 0°C. The reaction mixture was stirred overnight, and the solvent and bromoethane were removed under vacuum.

Reaction from Disodium Hypophosphate **2**. Disodium hypophosphate (0.5 g, 1.6 mmol) was suspended in a solution of hexamethyldisilazane (2.4 mL, 11 mmol) in dry dichloromethane (10 mL). Trimethylsilyl chloride (0.8 mL, 6.4 mmol) was added, and the reaction mixture was refluxed for 12 h. The solid was filtered off, and the volatile fractions were removed in vacuo. The remaining wax-like white solid **2** was used without further purification.

mp: 55–57°C. ^{1}H NMR (300.1 MHz, $CDCl_3$) δ (ppm): 0.34 (s, $^1J_{\text{CH}}$ = 120 Hz, 36H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ (ppm): 1.3 (s, $^1J_{\text{SiC}}$ = 1.7 Hz, 12C, CH_3). ^{29}Si NMR (59.6 MHz, $CDCl_3$) δ (ppm): 24.3 (s, $^2J_{\text{HSi}}$ = 6.9 Hz, 4Si). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ (ppm): −10.3 (s, 2P). IR (neat, ATR) ν cm^{-1}: 2965 (w), 2905 (w), 1418 (w), 1242 (s), 1092 (m), 1018 (s), 978 (s), 829 (s), 762 (s), 704 (m), 669 (m), 583 (w). MS: *m/z* 450 (M^+), 435, 314, 299, 211, 147, 73 (100%).

Alcoholysis of **3** *with Ethanol.* To a solution of **3** (40 mg) in CD_2Cl_2 (0.5 mL), an excess of ethanol (ca. 16 eq.) was added. A mixture of silylated hypophosphates and $EtOSiMe_3$ was identified by NMR spectroscopy of the reaction mixture.

$P_2O_2(OTMS)_x(OH)_y$: ^{1}H NMR (400.1 MHz, CD_2Cl_2) δ (ppm): 0.36 (br, CH_3Si). ^{13}C NMR (100.6 MHz, CD_2Cl_2) δ (ppm): 1.0 (br, CH_3Si).^{29}Si NMR (59.6 MHz, CD_2Cl_2) δ (ppm): 25.0 (br, CH_3Si). ^{31}P NMR (162.0 MHz, CD_2Cl_2) $x = 3$, $y = 1$: δ (ppm) = −9.7 (d, 1P), −2.7 (d, $^1J_{\text{PP}}$ = 826 Hz, 1P); $x = 2$, $y = 2$: δ (ppm) = −1.6 (s, 2P); $x = 1$, $y = 3$: δ (ppm) = −1.2 (d, 1P), 5.3 (d, $^1J_{\text{PP}}$ = 748 Hz, 1P); $x = 0$, $y = 4$: δ (ppm) = 5.9 (s, 2P).

Hydrolysis of **3**. A H_2O/THF mixture was slowly added to a solution of **3** in THF. **3** was cleanly hydrolyzed to hypophosphoric acid, which was identified by NMR spectroscopy.

$P_2O_2(OH)_4$: ^{1}H NMR (400.1 MHz, THF/H_2O) δ (ppm): 3.98 (br, 4H, OH). ^{31}P NMR (162.0 MHz, THF/H_2O) δ (ppm): 8.4 (s, 2P).

Synthesis of $[P_2O_2(OTMS)_3(O^-)] \times HDCHA^+$ **4a**

Dicyclohexylamine (0.22 mL, 1.12 mmol) and some grains of molecular sieves (4 Å) were added to a solution of **3** (460 mg, 1.02 mmol) in dichloromethane (10 mL). After stirring the reaction mixture for 6 h at 40°C, the product was identified by NMR spectroscopy.

^{1}H NMR (300.1 MHz, CD_2Cl_2) δ (ppm): 0.31 (s, 9H, CH_3), 0.36 (s, 18H, CH_3), 1.28 (br, 6H, $CH_{2,\text{cyc}}$), 1.66 (br, 6H, $CH_{2,\text{cyc}}$), 1.85 (br, 4H, $CH_{2,\text{cyc}}$), 2.13 (br, 4H, $CH_{2,\text{cyc}}$), 2.97 (br, 2H, CH_{cyc}), 9.57 (br, 2H, NH). ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ (ppm): 1.1 (br, 6C, CH_3), 1.3 (br, 3C, CH_3), 24.7 (br, 4C, $CH_{2,\text{cyc}}$), 24.9 (br, 2C, $CH_{2,\text{cyc}}$), 28.8 (br, 4C, $CH_{2,\text{cyc}}$), 52.5 (br, 2C, CH_{cyc}). ^{29}Si NMR (59.6 MHz, CD_2Cl_2) δ (ppm): 15.3 (s, $^2J_{\text{HSi}}$ = 8.8 Hz, 1Si), 19.7 (s, $^2J_{\text{HSi}}$ = 9.0 Hz, 2Si). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ (ppm): −7.2 (d, $^1J_{\text{PP}}$ = 748 Hz, 1P), 0.4 (d, $^1J_{\text{PP}}$ = 748 Hz, 1P).

Synthesis of $[P_2O_2(OTMS)_2(O^-)_2] \times 2HDCHA^+$ **5a**

To a solution of **3** (280 mg, 0.62 mmol) in dichloromethane (10 mL), dicyclohexylamine (0.24 mL, 1.4 mmol) and some grains of molecular sieves (4 Å) were added. The reaction mixture was stirred overnight at 40°C. A white solid precipitated. The solid was filtered off and washed with hexane.

^{1}H NMR (300.1 MHz, CD_2Cl_2) δ (ppm): 0.24 (s, 18H, CH_3), 1.29 (br, 12H, $CH_{2,\text{cyc}}$), 1.60 (br, 12H, $CH_{2,\text{cyc}}$), 1.83 (br, 8H, $CH_{2,\text{cyc}}$), 2.07 (br, 8H, $CH_{2,\text{cyc}}$), 2.85 (br, 4H, CH_{cyc}), 10.29 (br, 4H, NH). ^{13}C NMR

(75.5 MHz, CD_2Cl_2) δ (ppm): 1.4 (br, 6C, $\mathit{C}H_3$), 24.9 (br, 8C, $\mathit{C}H_{2,cyc}$), 25.3 (br, 4C, $\mathit{C}H_{2,cyc}$), 29.9 (br, 8C, $\mathit{C}H_{2,cyc}$), 52.9 (br, 4C, $\mathit{C}H_{cyc}$). ^{29}Si NMR (59.6 MHz, CD_2Cl_2) δ (ppm): 12.5 (s, $^2J_{HSi} = 10$ Hz, 2Si). ^{31}P NMR (121.5 MHz, CD_2Cl_2) δ (ppm): 4.2 (s, 2P). IR (neat, ATR) ν (cm^{-1}): 2934 (w), 2857 (w), 2485 (w), 2410 (w), 1511 (w), 1454 (w), 1384 (w), 1237 (w), 1177 (s) (P=O), 1104 (w), 1031 (w), 998 (w), 960 (s), 918 (m), 857 (w), 834 (s), 753 (m), 676 (w), 593 (w).

Synthesis of $[P_2O_2(OTMS)_2(O^-)_2] \times 2$ HDACH$^+$ **5d**

(*S*,*S*)-1,2-Diaminocyclohexane (178 mg, 1.56 mmol) was added to a solution of **3** (320 mg, 0.71 mmol) in chloroform (4 mL). The solution was stirred for 12 h in the presence of some grains of molecular sieves (4 Å) at 40°C. The solvent was slowly evaporated in vacuo until the product started to crystallize. The solution was kept under a static vacuum for 30 min to allow the colorless crystals of **5d** to grow. The solvent was decanted. The moisture sensitive crystals were characterized by NMR spectroscopy and an X-ray diffraction study.

^1H NMR (300.1 MHz, CD_2Cl_2) δ (ppm): 0.27 (s, 18H, $C\mathit{H}_3$), 1.32 (br, 8H, $C\mathit{H}_{2,cyc}$), 1.74 (br, 4H, $C\mathit{H}_{2,cyc}$), 2.03 (br, 4H, $C\mathit{H}_{2,cyc}$), 2.71 (br, 4H, $C\mathit{H}_{cyc}$), 5.87 (br, 10H, $N\mathit{H}$). ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ (ppm): 1.5 (s, 6C, $\mathit{C}H_3$), 24.8 (br, 4C, $\mathit{C}H_{2,cyc}$), 32.8 (br, 4C, $\mathit{C}H_{2,cyc}$), 55.1 (br, 4C, $\mathit{C}H_{cyc}$). ^{29}Si NMR (59.6 MHz, CD_2Cl_2) δ (ppm): 15.1 (s, $^2J_{HSi} = 7.5$ Hz, 2Si). ^{31}P NMR (121.5 MHz, CD_2Cl_2) δ (ppm): 3.4 (s, 2P).

Alcoholysis of $[P_2O_2(OTMS)_2(O^-)_2] \times 2$ HDCHA$^+$ **5a**

The dissolution of **5a** in a dichloromethane/ethanol solution or in pure ethanol took about 5 min. **5a** was slowly hydrolyzed (over 3 days) by ethanol yielding $EtOSiMe_3$, the diammonium salt $P_2O_2(OTMS)OH(O^-)_2 \times 2$H*DCHA*$^+$, and the diammonium salt of the hypophosphate **2**, $P_2O_2(OH)_2(O^-)_2 \times 2$H*DCHA*$^+$ (confirmed by ^{31}P and ^{29}Si NMR spectra of the reaction mixture).

5a: ^{29}Si NMR (59.6 MHz, CD_2Cl_2/ethanol) δ (ppm): 13.9 (s, 2Si). ^{31}P NMR (121.5 MHz, CD_2Cl_2/ethanol) δ (ppm): 2.0 (s, 2P).

$P_2O_2(OTMS)OH(O^-)_2 \times 2$H*DCHA*$^+$: ^{29}Si NMR (59.6 MHz, CD_2Cl_2/ethanol) δ (ppm): 14.6 (s, 1Si). ^{31}P NMR (121.5 MHz, CD_2Cl_2/ethanol) δ (ppm): 2.1 (d, 1P), 7.6 (d, $^1J_{PP} = 699$ Hz, 1P).

$P_2O_2(OH)_2(O^-)_2 \times 2$H*DCHA*$^+$: ^{31}P NMR (121.5 MHz, CD_2Cl_2/ethanol) δ (ppm): 8.6 (s, 2P).

Reaction of **3** *with KO^{t}Bu*

KO^{t}Bu (164 mg, 1.34 mmol) was added to a solution of **3** (300 mg, 0.67 mmol) in THF (40 mL), and the suspension was stirred for 1 h at room temperature. The precipitate was filtered, washed with dry THF, dried and analyzed. The obtained solid was insoluble in CH_2Cl_2, DMSO, very poorly soluble in THF. It was not further analyzed, but is probably the salt $P_2O_2(OTMS)_2(OK)_2$.

^{31}P NMR (121.5 MHz, THF) δ (ppm): 5 (br, 2P).

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