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Reductive Cleavage of the Halogen–Phosphorus and Sulfur–Phosphorus Bonds with Alkali Metals

Marek Stankiewicz, Jacek Nycz, and Janusz Rachon

Department of Organic Chemistry, Chemical Faculty, Technical University of Gdańsk, 80-952 Gdańsk, Poland

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ABSTRACT: *The reduction of thiophosphorus acid chlorides with alkali metals (Na, K) in liq.* NH_3*/THF solution, potassium anthracenide, and potassium naphthalenide was investigated. It was found that these types of phosphorus compounds easily undergo reduction to* $>P{-}S^-$ *anions. It was also demonstrated that* $>P{-}O^-$ *and* $>P{-}S^-$ *anions as well very efficiently undergo sulfurization with elementary sulfur in liquid ammonia to yield* $>P(O)S^-$ *and* $>P(S)S^-$ *anions, respectively.* © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:330–339, 2002; Published online in Wiley Interscience (www.interscience.wiley.com). DOI 10.1002/hc.10040

INTRODUCTION

The reductive cleavage of the $>P(Y){-}Cl$ [Y: O, S] bond is an interesting subject from the synthetic and mechanistic point of view. In our previous paper [1], we reported that phosphorus acid chlorides, as well as hypophosphates and pyrophosphates, easily undergo reduction to $>P{-}O^-$ and $>P(O){-}O^-$ anions, respectively, with alkali metals in liq. NH_3/THF solution and potassium naphthalenide in THF. Additionally, we were able to demonstrate that a mixed P(III)–P(V) anhydride is reduced by potassium naphthalenide in THF with the cleavage of the P(III)–oxygen bond.

The reactions of $>P(S)Cl$ compounds (thiophosphoric acid chlorides, thiophosphonic acid chlorides, thiophosphinic acid chlorides) with alkali metals are complex, and the data presented in the literature are often incompatible. For instance, Inamoto and co-workers [2] discovered that, in the attempted preparation of $Ph_2P{-}S^-$ from diphenylphosphinothioyl chloride and metal (Li or Na), desulfurization took place by use of excess amounts of metal or by heating for a long time. After treatment of diphenylphosphinothioyl chloride with magnesium in THF at 150°C, on the other hand, there was found in the reaction mixture a small amount of diphenylphosphinodithioic acid. On the basis of this observation, Inamoto and co-workers claimed that, for the desulfurization, a disproportionation process of $Ph_2P{-}S^-$ is responsible [2]. Moreover, Inamoto identified in the reaction mixture, after treatment of diphenylphosphinothioyl chloride with Li in THF at 150°C, diphenylphosphane oxide, tetramethylene bis(diphenylphosphinodithioate), and *S,S*-tetramethylene diphenylphosphinothioate diphenylphosphinodithioate [3].

On the other hand, Horner [4] was able to demonstrate that a phosphane sulfide can be reduced easily with sodium to the corresponding phosphane. Also, Issleib [5] reported that treatment of diphosphane disulfide with sodium in dioxan furnished the corresponding diphosphane or sodium phosphinide, depending on the structures of the starting materials and the conditions of the reaction. Reductive

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Correspondence to: Janusz Rachon; e-mail: rachon@altis.chem.pg.gda.pl.

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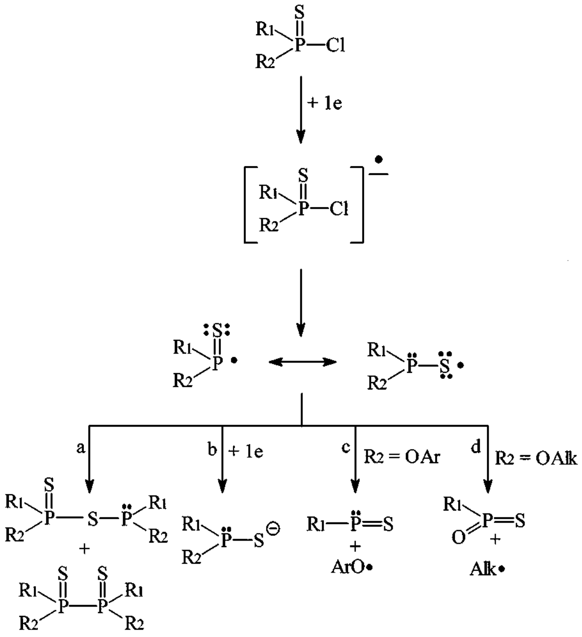
desulphurization of organosulfur compounds with sodium in liquid ammonia has been explored by Verkade [6]. He observed greater than 95% sulfur removal when dialkyl mono- or polysulfides were treated with Na in liquid ammonia. This procedure is only moderately successful for desulfurizing polycyclic aromatic sulfur compounds, but is quite efficient for dialkyl mono- or polysulfides, dialkyl sulfones, and trialkylphosphane sulfides. In contrast, triphenylphosphane sulphide yields diphenylphosphane (99%) in the reaction with sodium in liquid ammonia. The results of the last experiment strongly suggest that, in the case of the aromatic phosphane sulfide, desulphurization as well as the cleavage of the P—C bond occur. It should be mentioned at this point that liquid ammonia solutions of Li as well as Na are used for the reductive cleavage of the C—P bond in triphenylphosphanes [7]. On the other hand, it was reported that, in the reaction of sodium naphthalenide with diarylphosphinothioyl chlorides, the corresponding tetraaryldiphosphane disulfides are produced [8].

To the best of our knowledge, the reductive cleavage of the P—Cl bond in compounds of the >P(S)Cl type, particularly under homogenous conditions, has not been the subject of systematic studies. In connection with our interest in the reactivity of the acids of trivalent phosphorus, we initiated studies of the reaction between >P(S)Cl type compounds and electron donors (alkali metals in liquid ammonia, naphthalenide radical anion). The results of these studies are presented herein.

RESULTS AND DISCUSSION

As the thiophosphorus electrophilic reagents for our study, we chose the following compounds: 2-chloro-5,5-dimethyl-[1.3.2]dioxaphosphinane-2-sulphide, diethyl chlorothiophosphate, methyl phenylchlorothiophosphonate, diphenylphosphinothioyl chloride, and *t*-butylphenylphosphinothioyl chloride. These types of thiophosphorus electrophiles were treated with electron donors, namely, potassium naphthalenide in THF and sodium in liquid ammonia/THF mixture.

From the theoretical point of view, the >P(S)Cl electrophile can accept an electron to form a radical anion, which should collapse to a thiophosphonyl radical and chloride anion. According to the substituents on the phosphorus and the reaction conditions, the thiophosphonyl radical may (a) dimerize; (b) subsequently accept an electron, being reduced to >P—S⁻ anion; or (c) undergo further fragmentation (Scheme 1).

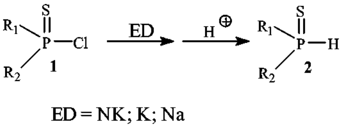


SCHEME 1

Additionally, the action of sodium in liquid ammonia can results in desulfurization and also a Birch reduction or cleavage of the P—C bond if an aromatic system is present in the starting material.

First, we carried out reduction experiments with potassium naphthalenide in THF. In the standard procedure the >P(S)Cl electrophiles are added to the tetrahydrofuran solution of potassium naphthalenide at −78°C. The dark-green color of the solution disappears in about half an hour after the addition of the last drop of the phosphorus electrophile. The reaction was quenched by addition of aqueous $KHSO_4$ solution at −78°C, and, after removal of the solvents, the products were isolated by radial chromatography. The results of this set of experiments are presented in Scheme 2 and collected in Table 1 (runs 1–6).

As one can see from the data collected in Table 1, all of the >P(S)Cl electrophiles (**1**) were reduced with two equivalents of potassium naphthalenide to the corresponding >P—S⁻ anion, which, after protonation, yielded a secondary phosphane sulfide or a dialkyl thiophosphate (**2**), respectively. We did not find in the reaction mixture compounds with a P—P bond (hypothiophosphates or diphosphane disulphide).



ED = NK; K; Na

SCHEME 2

TABLE 1 Reduction of the $R^1R^2P(S)Cl$ Type Electrophiles with Single Electron Donors (ED): Potassium Naphthalenide (NK) in THF or with Alkali Metals in Liquid Ammonia

Run	*R^1*	*R^2*	*ED*	*ED/>P(S)Cl*	*Isolated Yield (%)*	
					1	**2**
1	Ph	*t*-Bu	NK	1	53	37
2	Ph	*t*-Bu	NK	2		68
3	Ph	Ph	NK	2		71
4	*t*-Bu	*t*-Bu	NK	2		81
5	EtO	EtO	NK	2		62
6	$OCH_2C(CH_3)_2CH_2O$	$OCH_2C(CH_3)_2CH_2O$	NK	2		82
7	Ph	*t*-Bu	K	2		70
8	Ph	*t*-Bu	Na	2		78
9	*t*-Bu	*t*-Bu	K	2		80
10	EtO	EtO	K	2		67
11	$OCH_2C(CH_3)_2CH_2O$	$OCH_2C(CH_3)_2CH_2O$	K	2		72

The treatment of *t*-butylphenylthiophosphinyl chloride with one equivalent of potassium naphthalenide produced a low yield of the phosphane sulfide (**2**) (Scheme 2; $R^1 = t$-Bu, $R^2 = $ Ph). From this reaction mixture, we isolated *t*-butylphenylphosphane sulfide (37%) and starting material (53%). The starting material recovered from this reaction mixture strongly suggests that the thiophosphonyl radical undergoes a much faster one-electron reduction process to produce the >P–S⁻ anion than does the >P(S)Cl electrophile.

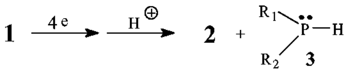
We also performed reduction experiments with alkali metal/NH_3/THF solution at −78°C. One equivalent of the >P(S)Cl type compound was added to the blue solution of two equivalents of alkali metal (Na, K) dissolved in the mixture of liquid NH_3: THF = 1:1. The blue color of the solution disappeared in a few minutes after the addition of the last drop of phosphorus electrophile. The reaction was quenched by solid NH_4Cl, and, after removal of the solvents, the products were isolated by radial chromatography (or by distillation). The results of this set of experiments are presented in Table 1 (runs 7–11).

Examination of the data collected in Table 1 (runs 1–6 and runs 7–11) shows that reduction of the >P(S)Cl electrophiles by alkali metal solution in liquid ammonia is superior to the use of potassium naphthalenide in THF. Additionally, the high yields of the *t*-butylphenylphosphane sulfide (Table 1, runs 7 and 8) show that the reduction of the P–Cl bond is a much faster process than the Birch reduction or the P–C bond cleavage observed under the same reaction conditions when triphenylphosphane is subjected to reduction. In the experiments where *t*-butylphenylphosphinothioyl chloride was the subject for the reduction by the action of a solution of alkali metal (sodium or potassium) in liquid ammonia/THF mixture, we noticed the characteristic odor of phosphane during the workup of the reaction mixture (Table 1, runs 7 and 8). This observation suggested that, during the reduction process, desulfurization can also take place.

We decided to verify this hypothesis by experiments in which the reduction of the >P(S)Cl electrophiles was carried out with four equivalents of a reducing agent (alkali metals/liquid ammonia, potassium naphthalenide, or potassium anthracenide). One equivalent of the >P(S)Cl type compound was added to the solution of four equivalents of a reducing agent, and, after 30 min, the reaction mixture was acidified and the products were isolated by radial chromatography (or by distillation). The results of this set of experiments are presented in Scheme 3 and collected in Table 2.

From the reaction mixture composed of one equivalent of phosphinothioyl chloride and four equivalents of potassium in liquid ammonia (Table 2, runs 12 and 13), after protonation, we isolated phosphane **3**, namely, *t*-butylphenylphosphane (74%) and diphenylphosphane (62%), respectively. By way of contrast, the treatment of 2-chloro-5,5-dimethyl-[1.3.2]dioxaphosphinane-2-sulfide with four equivalents of potassium in liquid ammonia (Table 2, run 14) resulted in the formation of 5,5-dimethyl-[1.3.2]dioxaphosphinane-2-sulfide.

On the other hand, from the reaction mixture composed of one equivalent of *t*-butylphenylphosphinothioyl chloride and four equivalents of potassium naphthalenide or potassium anthracenide



SCHEME 3

TABLE 2 Reduction of the $R^1R^2P(S)Cl$ Type Compounds with Four Equivalents of Potassium/Liquid Ammonia, Potassium Naphthalenide (NK), or Potassium Anthracenide (AK)

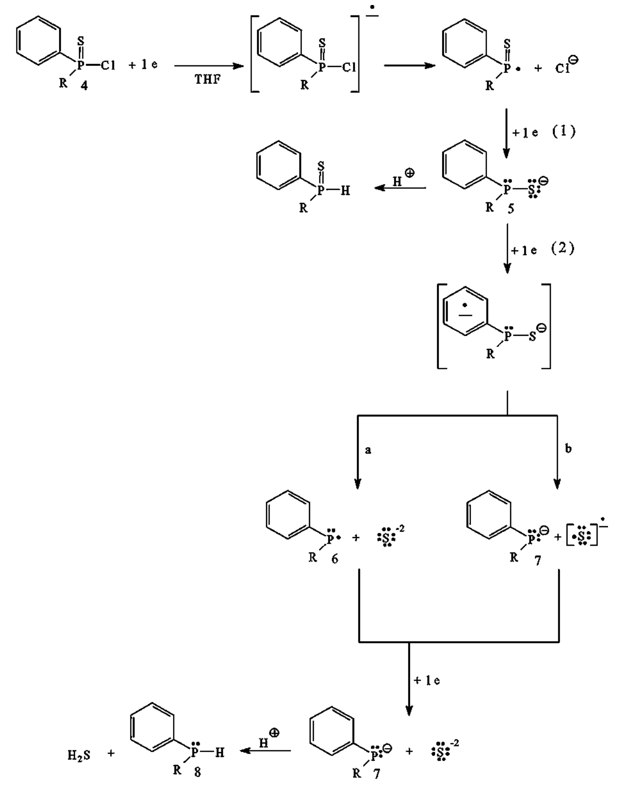
				Isolated Yield (%)	
Run	*R^1*	*R^2*	*Reducer*	**2**	**3**
12	Ph	*t*-Bu	K/NH_3		74
13	Ph	Ph	K/NH_3		62
14	$OCH_2C(CH_3)_2CH_2O$	$OCH_2C(CH_3)_2CH_2O$	K/NH_3	77	
15	Ph	*t*-Bu	NK	71	
16	Ph	*t*-Bu	AK	72	

(Table 2, runs 15 and 16) we isolated *t*-butylphenylphosphane sulfide (**2**, $R^1 = Ph$, $R^2 = t$-Bu). The results of this set of experiments show that, for the desulfurization process, the aromatic system as a moiety of the electrophile is necessary and this process requires a much higher reduction potential than that of dehalogenation. Also, the results of experiments strongly suggested that, in the first step, the >P(S)Cl electrophile is reduced to the $>P{-}S^-$ anion, which, if the aromatic system is present in the structure of the anion, can be further reduced to $>P^-$ and S^{2-} anions. Probably, the first process of reduction of the >P(S)Cl to the $>P{-}S^-$ anion is faster than that of desulfurization to the $>P^-$ anion. Furthermore, the second process, desulfurization, requires the presence of a group which contains π electrons with nearest connection to the phosphorus atom. Therefore, a phosphorus electrophile which contains π electrons (e.g., a phenyl group) is easily reduced to an $>P^-$ anion.

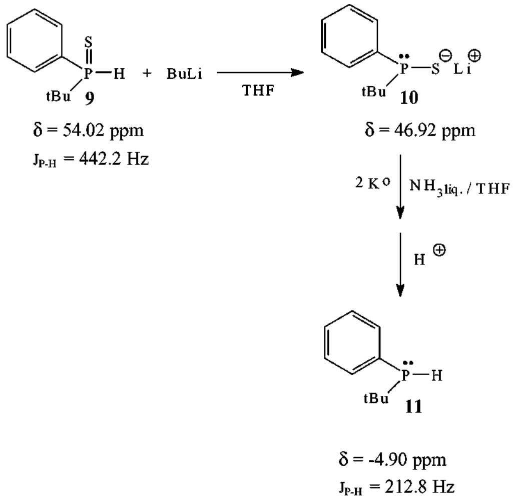
We have proposed a mechanism for the reduction and desulfurization of the >P(S)Cl electrophile (Scheme 4). In the first step of the reduction process of the >P(S)Cl electrophile **4**, the $>P{-}S^-$ anion **5** is generated (1). Transfer of an electron from a reducing agent (solution of alkali metal in liquid ammonia) into the LUMO of the acceptor (into the π^* orbital of the $>P{-}S^-$ anion **5**) leads to a radical dianion (2). Then the electron is transferred from the π^* orbital to the σ^* orbital of the $P{-}S^-$ bond to produce a frangible species (or transition state) which collapses with $P{-}S^-$ bond cleavage to form the phosphinyl radical **6** and sulfur anion (pathway "a") or to form the $>P^-$ anion **7** and sulfur radical anion (pathway "b"). Next, the phosphinyl radical is reduced to the $>P^-$ anion, or the sulfur radical anion is reduced to the sulfur anion S^{2-}. Therefore, pathway "a" or "b" provides the same products: the $>P^-$ anion and sulfur anion S^{2-}.

At this point, it was very important to check if the $>P{-}S^-$ anion is able to accept electrons and can be reduced into a $>P^-$ anion. In a separate experiment, we were able to demonstrate that the treatment of *t*-butylphenylthiophosphinide anion **10** ($\delta_{31P} = 46.92$ ppm; generated in the reaction of one equivalent of *t*-butylphenylphosphane sulfide **9** in THF with one equivalent of *n*-BuLi) with two equivalents of potassium in liquid ammonia produced only the *t*-butylphenylphosphinide anion. After protonation of this reaction mixture we isolated *t*-butylphenylphosphane **11** [$\delta_{31P} = -4.84$ ppm, $J_{P-H} = 212.67$ Hz] (Scheme 5) in 65% yield.

By way of contrast, after the treatment of 5,5-dimethyl-[1.3.2]dioxaphosphinane-2-sulfide anion **13** ($\delta_{31P} = 46.92$ ppm, generated from *n*-BuLi



SCHEME 4



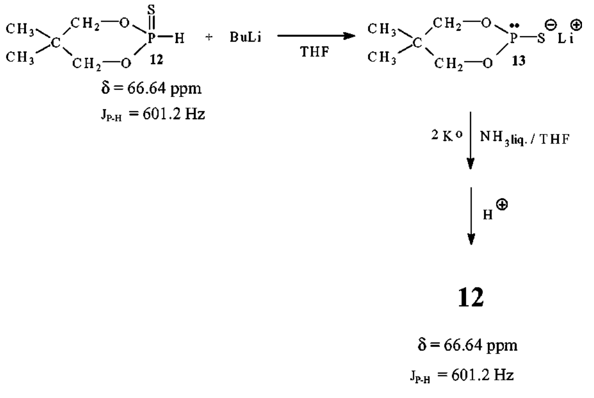
SCHEME 5

and 5,5-dimethyl-[1.3.2]dioxaphosphinane-2-sulfide **12**) with 2 equivalents of sodium in liquid ammonia, we isolated (after protonation) 5,5-dimethyl-[1.3.2]dioxaphosphinane-2-sulfide **12** (Scheme 6).

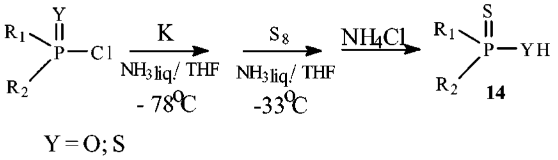
Sulfurization of the $>$P—O$^-$ and $>$P—S$^-$ Anions with Sulfur in Liquid Ammonia

Thioacids of various types of phosphorus acids are extremely important materials of commerce. Thio derivatives are used as pesticides, flotation agents, oil and gasoline additives, and rubber vulcanization accelerators. More recently, they have become important in studies on the chemical modification of natural phosphates, especially nucleotides.

Thioacids are formed when the chlorides are reacted with H_2S or NaSH. The P=O group in esters, as in phosphane oxides, can be replaced with sulfur by reaction with phosphorus pentasulfide or the Lawesson reagent. Another method of synthesis of monothio- and dithiophosphorus acids is based on the reaction of the $>$P(O)H acids or secondary phosphanes with elemental sulfur in the presence of base. In most cases, this reaction is performed at a temperature between 90 and 110°C [9].



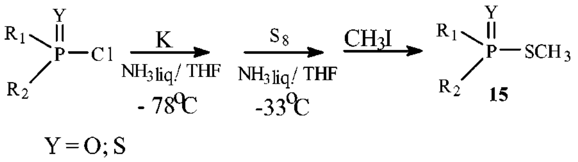
SCHEME 6



SCHEME 7

In the course of our study, we developed the method of generation of $>$P—O$^-$ as well as $>$P—S$^-$ anions in liquid ammonia. On the other hand, it is well known that elemental sulfur is soluble in liquid ammonia. We decided to check if these types of anions will react with elemental sulfur in liquid ammonia. In a series of experiments, we treated freshly generated ammonia solutions of the $>$P—O$^-$ as well as $>$P—S$^-$ anions (obtained from acid chlorides in the reduction process using potassium in liquid ammonia) with elemental sulfur (Scheme 7). The results of this set of experiments are collected in Table 3.

As one can see from the data collected in Table 3, the $>$P—O$^-$ as well as $>$P—S$^-$ anions very efficiently undergo sulfurization with elemental sulfur in liquid ammonia to yield monothio- as well as dithiophosphorus anions, respectively. The one-pot procedure is very simple: the addition of elemental sulfur into the solution of the $>$P—O$^-$ as well as $>$P—S$^-$ anions in liquid ammonia (freshly obtained from acid chlorides in the reduction process using potassium in liquid ammonia) furnished, in 30 min at −33°C, the desired ammonium salts of the monothio- or dithiophosphorus acids, respectively. Moreover, we were also able to demonstrate that ammonium salts obtained according to this procedure can be used without further purification in the alkylation processes. The acid chlorides were reduced with potassium in liquid ammonia/THF solution, and then the reaction mixture was treated with elemental sulfur (sulfur is readily soluble in the solvent system liq. NH_3/THF above −40°C). After evaporation of the liquid ammonia, the residue was diluted with THF, methyl iodide was added, and the methyl esters were isolated. The results of this set of experiments are presented in Scheme 8 and collected in Table 4. As one can see from the data collected in Table 4, our method appears to be a promising one; starting from the acid chlorides in simple procedures we obtained methyl esters **15** in very high yields.



SCHEME 8

EXPERIMENTAL

Tetrahydrofuran, benzene, hexane, and toluene were dried with sodium–potassium alloy. Melting points are uncorrected. ^{31}P NMR and ^{1}H NMR spectra were recorded with a Varian FT NMR spectrometer at 200 or 500 MHz. Potassium naphthalenide (anthracenide) was prepared from potassium and naphthalene (anthracene) in dry THF under argon and with protection from oxygen before its use [10].

Some of the compounds which have been used were produced as follows: *t*-butylphenylphosphinothioyl chloride was obtained according to the known procedure [11], b.p. 100–104°C/0.04 mm Hg, m.p. = 71–73°C, ^{1}H NMR (CDCl$_3$) $\delta = 1.15$ (d, $^{3}J_{\mathrm{P\text{–}H}} = 19$ Hz, *t*-Bu, 9H), 7.10–7.77 (m, aromat, 5H), ^{31}P NMR (CDCl$_3$) $\delta = 115.27$ ppm, di-*t*-butylphosphinothioyl chloride was obtained according to the known procedure [12], eluted with chloroform, ^{1}H NMR (CDCl$_3$) $\delta = 1.47$ (d, $^{3}J_{\mathrm{P\text{–}H}} = 18$ Hz, 2 *t*-Bu, 18H), ^{31}P NMR (CDCl$_3$) $\delta = 146.16$ ppm, diphenylphosphinothioyl chloride was obtained according to the known procedure [13], b.p. 156°C/0.01 mm Hg, ^{31}P NMR (CDCl$_3$) $\delta = 81.4$ ppm, 2-chloro-2-thiono-5,5-dimethyl-[1.3.2]-dioksafosfinan was obtained according to the known procedure [14], ^{31}P NMR (CDCl$_3$) $\delta = 59.42$ ppm.

Reduction of the $R^1R^2P(S)Cl$ Type Phosphorus Compounds

Reduction of the $R^1R^2P(S)Cl$ Type Phosphorus Compounds with Potassium Naphthalenide in THF. General procedure for runs 1–6: Into the freshly prepared potassium naphthalenide (from 1.410 g of naphthalene and 0.390 g of potassium) in 25 cm^3 of THF at −78°C, 10 mmol (run 1) or 5 mmol (runs 2–6) of each phosphorus electrophile (*t*-butylphenylphosphinothioyl chloride, diphenylphosphinothioyl chloride, diethyl chlorothiophosphate, 2-chloro-5,5-dimethyl-[1.3.2]-dioxaphosphinane-2-sulphide) in 5 cm^3 of THF was added. After disappearance of the dark-green color of the reaction mixture, benzene (200 cm^3) and an aqueous KHSO$_4$ solution (5 cm^3) were added. The aqueous layer was extracted with benzene, and the combined organic layers were dried over MgSO$_4$. The solvent was removed in vacuum, and the products were separated by radial chromatography. Naphthalene was eluted with hexane, the reduction products with CHCl$_3$ (Table 1, runs 1–6).

Run 1: naphthalene 1.314 g (10 mmol, 93%); *t*-butylphenylphosphinothioyl chloride (eluted with chloroform) 1.234 g (5.3 mmol, 53%), ^{1}H NMR (CDCl$_3$) $\delta = 1.13$ (d, $^{3}J_{\mathrm{P\text{–}H}} = 20$ Hz, *t*-Bu, 9H), 7.03–7.83 (m, aromat, 5H). ^{31}P NMR (CDCl$_3$) $\delta = 115.00$ ppm; *t*-butylphenylphosphane sulfide (eluted with chloroform) 0.734 g (3.7 mmol, 37%), ^{1}H NMR (CDCl$_3$) $\delta = 1.10$ (d, $^{3}J_{\mathrm{P\text{–}H}} = 16$ Hz, *t*-Bu, 9H), 6.58 (d, $J_{\mathrm{P\text{–}H}} = 442$ Hz, PH, 1H), 6.80–7.56 (m, aromat, 5H), ^{31}P NMR (CDCl$_3$) $\delta = 53.9$ ppm.

Run 2: naphthalene 1.293 g (10 mmol, 92%); *t*-butylphenylphosphane sulfide 0.671 g (3.4 mmol, 68%).

Run 3: naphthalene 1.311 g (10.2 mmol, 93%); diphenylphosphane sulfide 0.769 g (3.1 mmol, 71%), ^{1}H NMR (CDCl$_3$) $\delta = 7.48$–7.82 (m, aromat, 10 H), 8.05 (d, $J_{\mathrm{P\text{–}H}} = 467$ Hz, PH, 1H), ^{31}P NMR (CDCl$_3$) $\delta = 23.4$ ppm.

Run 4: naphthalene 1.308 g (10.2 mmol, 93%); di-*t*-butylphosphane sulfide 0.722 g (4.0 mmol, 81%), ^{1}H NMR (CDCl$_3$) $\delta = 1.26$ (d, $^{3}J_{\mathrm{P\text{–}H}} = 16$ Hz, 2 *t*-Bu, 18H), 6.58 (d, $J_{\mathrm{P\text{–}H}} = 418$ Hz, PH, 1H), ^{31}P NMR (CDCl$_3$) $\delta = 76.3$ ppm.

Run 5: naphthalene 1.176 g (9.2 mmol, 84%); *O,O′*-diethyl thiophosphate 0.479 g (3.1 mmol, 62%), ^{1}H NMR (CDCl$_3$) $\delta = 1.18$ (t, $^{3}J_{\mathrm{H\text{–}H}} = 6$ Hz, CH$_3$, 6H), 3.87 (dq, $^{3}J_{\mathrm{H\text{–}H}} = 10$ Hz, $^{3}J_{\mathrm{P\text{–}H}} = 3$ Hz, CH$_2$, 4H), 7.57 (d, $J_{\mathrm{P\text{–}H}} = 648$ Hz, PH, 1H), ^{31}P NMR (CDCl$_3$) $\delta = 70.1$ ppm.

TABLE 3 Synthesis of Monothio- and Dithiophosphorus Acids

Run	R^1	R^2	*Y*	*Yield of* **14** *(%)*
17	EtO	EtO	O	62
18	*i*-PrO	*i*-PrO	O	82
19	OCH$_2$C(CH$_3$)$_2$CH$_2$O	OCH$_2$C(CH$_3$)$_2$CH$_2$O	O	78
20	Ph	*t*-Bu	O	95
21	EtO	EtO	S	66
22	OCH$_2$C(CH$_3$)$_2$CH$_2$O	OCH$_2$C(CH$_3$)$_2$CH$_2$O	S	81
23	Ph	*t*-Bu	S	85

TABLE 4 Synthesis of Monothio- and Dithiophosphorus Acid Methyl Esters

Run	*R^1*	*R^2*	*Y*	*Yield of* **15** *(%)*
24	Ph	*t*-Bu	O	82
25	Ph	*t*-Bu	O	85
26	EtO	EtO	S	85
27	$OCH_2C(CH_3)_2CH_2O$	$OCH_2C(CH_3)_2CH_2O$	S	94

Run 6: naphthalene 1.176 g (9.2 mmol, 84%); 5,5-dimethyl-[1.3.2]dioxaphosphinane-2-sulfide 0.681 g (1 mmol, 82%), ^{1}H NMR ($CDCl_3$) $\delta = 0.77$ (s, CH_3, 3H), 1.17 (s, CH_3, 3H), 3.50–10 (m, CH_2, 4H), 7.58 (d, $J_{P\text{–}H} = 601$ Hz, PH, 1H), ^{31}P NMR ($CDCl_3$) $\delta = 67.2$ ppm.

Reduction of the $R^1R^2P(S)Cl$ Type Phosphorus Compounds with Alkali Metals in Liquid Ammonia in the Molar Ratio 1:2. General procedure for runs 7–10: Alkali metal (10 mmol) was added to the mixture composed of liquid ammonia (25 cm^3) and THF (25 cm^3). The reaction mixture was stirred until complete dissolution of the alkali metal was realized; it was then cooled to −78°C, and 5 mmol of each chlorothiophosphorus compound (*t*-butylphenylphosphinothioyl chloride, diethyl chlorothiophosphate, 2-chloro-5,5-dimethyl-[1.3.2]-dioxaphosphinane-2-sulphide) in 5 cm^3 of THF was added. The reaction mixture was stirred at −78°C. The blue color of the solution disappeared in a few minutes after the addition of the last drop of phosphorus electrophile. Then 1.5 g of NH_4Cl was added and the ammonia was evaporated at 10 mm Hg. The residue was poured into a mixture of toluene and aqueous $KHSO_4$ solution. The water layer was extracted with toluene and the combined organic phase was dried over $MgSO_4$. The solvent was removed in vacuum and the products were separated by radial chromatography. The reduction products were eluted with $CHCl_3$ (Table 1, runs 7–11).

Run 7: *t*-butylphenylphosphane sulfide 0.694 g (3.5 mmol, 70%).
Run 8: *t*-butylphenylphosphane sulfide 0.773 g (3.9 mmol, 78%).
Run 9: di-*t*-butylphosphane sulfide 0.714 g (4.0 mmol, 80%).
Run 10: *O,O′*-diethyl thiophosphate 0.515 g (3.3 mmol, 67%).
Run 11: 5,5-dimethyl-[1.3.2]dioxaphosphinane-2-sulfide 0.598 g (3.6 mmol, 72%).

Reduction of the $R^1R^2P(S)Cl$ Type Phosphorus Compounds with Alkali Metals in Liquid Ammonia in the Molar Ratio 1:4. General procedure for runs 12–14: Alkali metal (20 mmol) was added to the mixture composed of liquid ammonia (25 cm^3) and THF (25 cm^3). The reaction mixture was stirred up to the point of complete dissolution of the alkali metal, then cooled to −78°C, and 5 mmol of each chlorothiophosphorus compound (*t*-butylphenylphosphinothioyl chloride, diphenylphosphinothioyl chloride, 2-chloro-5,5-dimethyl-[1.3.2]dioxaphosphinane-2-sulphide) in 5 cm^3 of THF was added. The reaction mixture was stirred at −78°C for 30 min. Then, 0.45 g (8.4 mmol) of NH_4Cl was added and the ammonia was evaporated at 10 mm Hg. The products were distilled (Table 2; runs 12 and 13) or poured into the mixture of toluene and aqueous $KHSO_4$ solution. The water layer was extracted with toluene and the combined organic phase was dried over $MgSO_4$. The solvent was removed in vacuum, and the products were separated by radial chromatography (Table 2; run 14)

Run 12: *t*-butylphenylphosphane (Kugelrohr, 60–61°C/0.9 mm Hg) 0.615 g (3.7 mmol, 74%), ^{1}H NMR ($CDCl_3$) $\delta = 1.00$ (d, $^3J_{P\text{–}H} = 12$ Hz, *t*-Bu, 9H), 5.60 (d, $J_{P\text{–}H} = 209$ Hz, PH, 1H), 6.60–7.43 (m, aromat, 5H), ^{31}P NMR ($CDCl_3$) $\delta = -4.84$ ppm.
Run 13: diphenylphosphane (Kugelrohr, 60–61°C/0.9 mm Hg) 0.577 g (3.10 mmol, 62%), ^{1}H NMR ($CDCl_3$) $\delta = 4.93$ (d, $J_{P\text{–}H} = 208$ Hz, PH, 1H), 6.57–7.33 (m, aromat, 10H), ^{31}P NMR ($CDCl_3$) $\delta = -39.9$ ppm.
Run 14: 5,5-dimethyl-[1.3.2]dioxaphosphinane-2-sulfide (eluted with chloroform) 0.640 g (3.85 mmol, 77%), ^{1}H NMR ($CDCl_3$) $\delta = 0.77$ (s, CH_3, 3H), 1.17 (s, CH_3, 3H), 3.50–4.10 (m, CH_2, 4H), 7.58 (d, $J_{P\text{–}H} = 601$ Hz, PH, 1H), ^{31}P NMR ($CDCl_3$) $\delta = 67.2$ ppm.

Reduction of the $R^1R^2P(S)Cl$ Type Phosphorus Compounds with Potassium Naphthalenide or Potassium Anthracenide in the Molar Ratio 1:4. General procedure for runs 15 and 16: Into the freshly prepared potassium naphthalenide (from 1.410 g of naphthalene and 0.390 g of potassium) or anthracenide (from 1.960 g of anthracene and 0.390 g of potassium) in 50 cm^3 of THF at −78°C, 2.5 mmol of the *t*-butylphenylphosphinothioyl chloride in 5 cm^3 of THF was added. The reaction mixture was stirred at −78°C for an hour, and then a mixture composed of 200 cm^3 of benzene and 10 cm^3 aqueous $KHSO_4$ solution was added. The aqueous layer was extracted with benzene and the combined organic layers were dried over $MgSO_4$. The solvent was removed in vacuum and the products were separated by radial chromatography (Table 2, runs 15 and 16).

Run 15: *t*-butylphenylphosphane sulfide (eluted with chloroform) 0.352 g (1.8 mmol, 71%), ^{1}H NMR ($CDCl_3$) $\delta = 1.10$ (d, $^3J_{P\text{–}H} = 16$ Hz, *t*-Bu, 9H), 6.58 (d, $J_{P\text{–}H} = 442$ Hz, PH, 1H), 6.80–7.56 (m, aromat, 5H), ^{31}P NMR ($CDCl_3$) $\delta = 53.9$ ppm.
Run 16: *t*-butylphenylphosphane sulfide (eluted with chloroform) 0.357 g (1.8 mmol, 72%).

Reduction of the Lithium t-Butylphenylthiophosphane Sulphide with Potassium in Liquid Ammonia in the Molar Ratio 1:2

Into the solution of 5 mmol of *t*-butylphenylphosphane sulphide in 5 cm^3 of THF at −78°C, 2.5 cm^3 of a 2 M solution of BuLi in cyclohexane (5 mmol) was added. After 30 min, a sample of the reaction mixture was removed, C_6D_6 was added, and the ^{31}P NMR spectrum was recorded. The ^{31}P NMR spectrum of the reaction mixture showed one resonance line attributable to lithium *t*-butylphenylthiophosphane ($\delta_{31P} = 46.92$ ppm). Next, the solution of the lithium *t*-butylphenylthiophosphane sulphide in THF was dropped into a solution of the potassium in liquid ammonia (0.390 g of potassium in 50 cm^3 of ammonia–THF mixture) at −78°C. The reaction mixture was stirred for 30 min, and then 0.45 g of NH_4Cl was added. Ammonia was removed in vacuum and the residue was distilled; *t*-butylphenylphosphane (Kugelrohr, 60–61°C/0.9 mm Hg) 0.515 g (3.1 mmol, 62%).

Attempted Reduction of the Lithium 5,5-Dimethyl-[1.3.2]dioxaphosphinane-2-sulfide with Potassium in Liquid Ammonia in the Molar Ratio 1:2

Into the solution of 5 mmol of 5,5-dimethyl-[1.3.2]dioxaphosphinane-2-sulfide in 5 cm^3 of THF at −78°C, 2.5 cm^3 of a 2 M solution of BuLi in cyclohexane (5 mmol) was added. Next, the solution of lithium 5,5-dimethyl-[1.3.2]dioxaphosphinane-2-thiolate in THF was dropped into the solution of potassium in liquid ammonia (0.390 g of potassium in 50 cm^3 of ammonia–THF mixture) at −78°C. After 30 min, 0.45 g (8.4 mmol) of NH_4Cl was added. Ammonia was removed in vacuum and a sample of the reaction mixture was taken off, and after addition of aqueous $KHSO_4$ solution and C_6D_6, the ^{31}P NMR spectrum was recorded. The ^{31}P NMR spectrum of the crude reaction mixture showed one resonance line attributable to 5,5-dimethyl-[1.3.2]dioxaphosphinane-2-sulfide ($\delta_{31} = 66.64$ ppm, $J_{P\text{–}H} = 601.2$ Hz). The product was isolated by radial chromatography; 5,5-dimethyl-[1.3.2]dioxaphosphinane-2-sulfide (eluted with chloroform), 0.614 g (3.70 mmol, 74%).

Sulfurization of the >P–O⁻ and >P–S⁻ Anions with Sulfur in Liquid Ammonia

The Synthesis of Mono- and Dithiophosphorus Acids. General procedure for runs 17–23: Potassium (0.39 g, 10 mmol) was added to the mixture composed of liquid ammonia (25 cm^3) and THF (25 cm^3). The reaction mixture was stirred up to the complete dissolution of alkali metal, then cooled to −78°C, and 5 mmol of each chlorophosphorus compound (diethyl chlorophosphate, diisopropyl chlorophosphate, 2-chloro-5,5-dimethyl-[1.3.2]dioxaphosphinane, *t*-butylphenylphosphinoyl chloride, *O,O′*-diethyl chlorothiophosphate, 2-chloro-5,5-dimethyl-[1.3.2]-dioxaphosphinane-2-sulphide, *t*-butylphenylphosphinothioyl chloride) in 5 cm^3 of THF was added. The reaction mixture was stirred at −78°C. The blue color of the solution disappeared in a few minutes after the addition of the last drop of the phosphorus electrophile. Then, 0.192 g of sulfur was added, the cooling bath was removed, and the reaction mixture was stirred at −33°C for 30 min. The ammonia was evaporated at 10 mm Hg. The residue was poured into a mixture of toluene and aqueous K_2CO_3 solution. The water layer was acidified with hydrochloric acid. Then, water was evaporated at 10 mm Hg, and the residue was extracted with 200 cm^3 of CH_2Cl_2. The organic phase was dried over $MgSO_4$. The solvent was removed under a vacuum and the products were separated (Table 3, runs 17–23).

Run 17: thiophosphoric acid *O,O′*-diethyl ester 0.527 g (3.1 mmol, 62%), ^{1}H NMR ($CDCl_3$) $\delta = 1.23$ (t, $^3J_{H\text{–}H} = 7$ Hz, CH_3, 6H), 3.45–4.28 (m, CH_2, 4H), 8.70 (s, OH, 1H), ^{31}P NMR ($CDCl_3$) $\delta = 64.21$ ppm.
Run 18: thiophosphoric acid *O,O′*-diisopropyl ester 0.812 g (4.1 mmol, 82%), ^{1}H NMR ($CDCl_3$) $\delta = 1.27$ (d, $^3J_{H\text{–}H} = 10$ Hz, CH_3, 12H), 4.20–4.87 (m, CH, 2H), 8.70 (s, OH, 1H), ^{31}P NMR ($CDCl_3$) $\delta = 58.50$ ppm.
Run 19: 2-hydroxy-5,5-dimethyl-2-thio-[1.3.2]-dioxaphosphinane 0.710 g (3.9 mmol, 78%), ^{1}H NMR ($CDCl_3$) $\delta = 1.00$ (s, CH_3, 3H), 1.12 (s, CH_3, 3H),

3.95 (s, CH_2, 4H), 4.60 (s, SH, 1H), ^{31}P NMR ($CDCl_3$) $\delta = 57.93$ ppm.

Run 20: *t*-butylphenylphosphinothioic acid 1.017 g (4.8 mmol, 71%), m.p. = 124–126°C, ^{1}H NMR ($CDCl_3$) $\delta = 1.13$ (d, $^3J_{P\text{–}H} = 17$ Hz, CH_3, 9H), 3.50 (s, SH, 1H), 6.60–7.51 (m, aromat, 5H), ^{31}P NMR ($CDCl_3$) $\delta = 94.85$ ppm.

Run 21: dithiophosphoric acid *O,O′*-diethyl ester 0.615 g (3.3 mmol, 66%), ^{1}H NMR ($CDCl_3$) $\delta = 1.24$ (t, $^3J_{H\text{–}H} = 7$ Hz, CH_3, 6H), 3.53–4.18 (m, CH_2, 4H), 3.28 (s, SH, 1H), ^{31}P NMR ($CDCl_3$) $\delta = 83.91$ ppm.

Run 22: 2-thiolo-2-thiono-5,5-dimethyl-[1.2.3]-dioxaphosphinane 0.802 g (4.0 mmol, 81%), ^{1}H NMR ($CDCl_3$) $\delta = 1.03$ (s, CH_3, 6H), 3.82 (d, $^2J_{H\text{–}H} = 14$ Hz, CH_2, 4H), 3.58 (s, SH, 1H), ^{31}P NMR ($CDCl_3$) $\delta = 69.04$ ppm.

Run 23: *t*-butylphenylphosphinodithioic acid 0.978 g (4.2 mmol, 85%), m.p. = 71–72°C, ^{1}H NMR ($CDCl_3$) $\delta = 1.13$ (d, $^3J_{P\text{–}H} = 18$ Hz, CH_3, 9H), 2.93 (s, SH, 1H), 6.80–7.80 (m, aromat, 5H), ^{31}P NMR ($CDCl_3$) $\delta = 85.82$ ppm.

Synthesis of Monothio- and Dithiophosphorus Acids Methyl Esters. General procedure for runs 24–27: Potassium (0.390 g, 10 mmol) was added to the mixture composed of liquid ammonia (25 cm^3) and THF (25 cm^3). The reaction mixture was stirred up to the complete dissolution of the alkali metal, then cooled to −78°C, and 5 mmol of each chlorophosphorus compound (*t*-butylphenylphosphinoyl chloride, *t*-butylphenylphosphinothioyl chloride, diethyl chlorothiophosphate, 2-chloro-5,5-dimethyl-[1.3.2]-dioxaphosphinane-2-sulphide) in 5 cm^3 of THF was added. The reaction mixture was stirred at −78°C. The blue color of the solution disappeared in a few minutes after the addition of the last drop of phosphorus electrophile. Then, 0.192 g of sulfur was added and the cooling bath was removed, the reaction mixture being stirred at −33°C for 30 min. Next, the ammonia was evaporated at 10 mm Hg. The residue was diluted with 25 cm^3 of THF. Then, 5 cm^3 of methyl iodide was added and the reaction mixture was stirred at room temperature for 3 h. The methyl esters were separated by radial chromatography (Table 4, runs 24–27).

Run 24: *S*-methyl-*t*-butylphenylphosphinothioate (eluted with $CHCl_3$) 0.936 g (4.1 mmol, 82%), ^{1}H NMR ($CDCl_3$) $\delta = 1.16$ (d, $^3J_{P\text{–}H} = 17$ Hz, CH_3, 9H), 2.15 (d, $^3J_{P\text{–}H} = 12$ Hz, CH_3, 3H), 6.83–7.93 (m, aromat, 5H), ^{31}P NMR ($CDCl_3$) $\delta = 69.40$ ppm.

Run 25: *S*-methyl-*t*-butylphenylphosphinodithioate (eluted with $CHCl_3$) 1.038 g (4.2 mmol, 85%), ^{1}H NMR $\delta = 1.10$ (d, $^3J_{P\text{–}H} = 17$ Hz, CH_3, 9H), 2.03 (d, $^3J_{P\text{–}H} = 12$ Hz, CH_3, 3H), 6.80–7.80 (m, aromat, 5H), ^{31}P NMR ($CDCl_3$) $\delta = 94.83$ ppm.

Run 26: *S*-methyl-*O,O′*-diethyldithiophosphate (eluted with $CHCl_3$) 0.807 g (4.2 mmol, 85%), ^{1}H NMR $\delta = 1.31$ (t, $^3J_{H\text{–}H} = 7$ Hz, CH_3, 6H), 2.25 (d, $^3J_{P\text{–}H} = 16$ Hz, CH_3, 3H), 4.23 (dq, $^3J_{H\text{–}H} = 7$ Hz, $^3J_{P\text{–}H} = 11$ Hz, CH_2, 4H), 6.83–7.93 (m, aromat, 5H), ^{31}P NMR ($CDCl_3$) $\delta = 93.25$ ppm.

Run 27: 5,5-dimethyl-2-(methylthio)-[1.3.2]-dioxaphosphorinane-2-sulfide (eluted with $CHCl_3$) 0.996 g (4.7 mmol, 94%), ^{1}H NMR ($CDCl_3$) $\delta = 0.93$ (s, CH_3, 3H), 1.12 (s, CH_3, 3H), 2.34 (d, $^3J_{P\text{–}H} = 17$ Hz, CH_3, 3H) 3.94 (m, CH_2, 4H), ^{31}P NMR ($CDCl_3$) $\delta = 86.42$ ppm.

CONCLUSION

It was found that the acid chlorides of the type $>P(S)Cl$ undergo reduction with sodium and potassium in liquid ammonia to provide the corresponding $>P{-}S^-$ anions. Moreover, the reduction process is much faster than ammonolysis. If, in the acid chloride, an aromatic moiety is connected to the phosphorus atom, reduction and desulfurization processes occur under the action of potassium in liquid ammonia. Radical anions of aromatic hydrocarbons can also reduce $>P(S)Cl$ chlorides to $>P{-}S^-$ anions, but, in contrast to potassium in liquid ammonia, desulfurization does not occur, and this was rationalized on the basis of redox potentials. We were able to demonstrate that $>P{-}O^-$ as well as $>P{-}S^-$ anions obtained in such a procedure can undergo sulfurization with elemental sulfur in liquid ammonia to provide $>P(O)S^-$ and $>P(S)S^-$ anions, respectively, which can be used for further syntheses without purification.

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