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Benign and High-Yielding, Large-Scale Synthesis of Diphenylphosphinodithioic Acid and Related Compounds

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Supporting Information

ABSTRACT: Diphenylphosphinodithioic acid (**6b**) and its triethyl ammonium salt (**6a**) were prepared by two new synthetic pathways, each employing cheap and readily available starting materials. These facile one-pot reactions were conducted on a kilogram scale and produced the desired products in high yield and quality, thereby surpassing all previously known routes. The synthesis of triethyl ammonium salts of 6*H*-dibenzo[*c*,*e*][1,2]oxaphosphinine-6-thiolate 6-sulfide (**3a**) was also further improved.

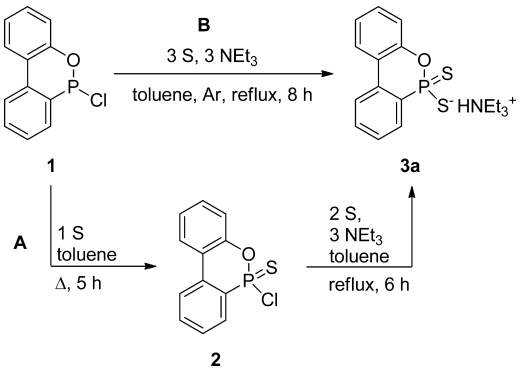
INTRODUCTION

Diphenylphosphinodithioic acid (DPPA, **6b**) and its derivatives are utilized for a plethora of different applications: DPPA is used as a chelating agent that can bind to different metals such as copper(I), actinides(III), and metals of the platinum group.[1−5] The difference in the coordination chemistry of DPPA and its derivatives between lanthanides(III) and actinides(III) enables these compounds to extract e.g. *Cm*(III) and Am(III) from lanthanides(III) in the advanced processing of spent nuclear fuel.[1−3] Metals of the platinum group can also be solvent extracted through coordination with **6b**.[4] Multimetal complexes of diphenylphosphinodithioic acid with copper(I) find application as antioxidation additives and in biological systems.[5] Furthermore, **6b** can be used as a corrosion inhibitor in photochemically cross-linkable coatings,[6,7] as a curing accelerator for epoxy resins,[8] and as a cross-linking agent for rubber polymers.[9] Recently, diphenylphosphinodithioic acid and some derivatives have been reported as flame retardants for polystyrene foams.[10] The mono- and di-sulfur-bridged derivatives **8a** and **8b** also find application as UV-stabilizers in polyolefins.[11] Despite the many different applications, no truly convenient synthesis has been published to the present day. The majority of preparations utilize a previously reported procedure.[12] While this method represents a reliable and feasible pathway towards **6b**, it suffers from several drawbacks, including the use of a huge excess of $AlCl_3$ and moderate yields. Yet for an industrial application, a cheap and easily scalable synthesis is crucial. In this work we present two new and convenient routes for the synthesis of triethyl ammonium diphenylphosphinodithioate (**6a**) and diphenylphosphinodithioic acid (DPPA, **6b**), respectively. In addition, we present an improved synthesis of the related compounds **3a** (triethyl ammonium 6*H*-dibenzo[*c*,*e*][1,2]oxaphosphinine-6-thiolate 6-sulfide) and **3b** (6-mercapto-6*H*-dibenzo[*c*,*e*][1,2]-oxaphosphinine 6-sulfide) which recently became of interest in the context of phosphinothioyl applications.[13]

RESULTS AND DISCUSSION

Synthesis of Triethyl Ammonium 6*H*-Dibenzo[*c*,*e*]-[1,2]oxaphosphinine-6-thiolate 6-Sulfide (3a). Recently, the synthesis of **3a** via sulfidation of 6-chloro-6*H*-dibenzo[*c*,*e*]-[1,2]oxaphosphinine (**1**) to form 6-chloro-6*H*-dibenzo[*c*,*e*]-[1,2]oxaphosphinine 6-sulfide (**2**) and its subsequent conversion with elemental sulfur and triethyl amine (route **A**, Scheme 1) has been described.[14] However, it has now been found that the initial sulfidation of **1** does not necessarily need to be carried out in a separate reaction step. Instead, feasibility of a one-pot reaction was demonstrated which is advantageous with respect to synthetic effort and reaction time (route **B**, Scheme 1). Therefore, 3 equiv of elemental sulfur and 3 equiv of triethyl amine were placed together with **1** and toluene in a round-bottomed flask under argon atmosphere and heated for 8 h at solvent reflux temperature. The progress of the reaction was monitored via ^{1}H- and ^{31}P NMR spectroscopy. NMR

Scheme 1. Synthesis of 3a: two-step and one-pot reaction pathway



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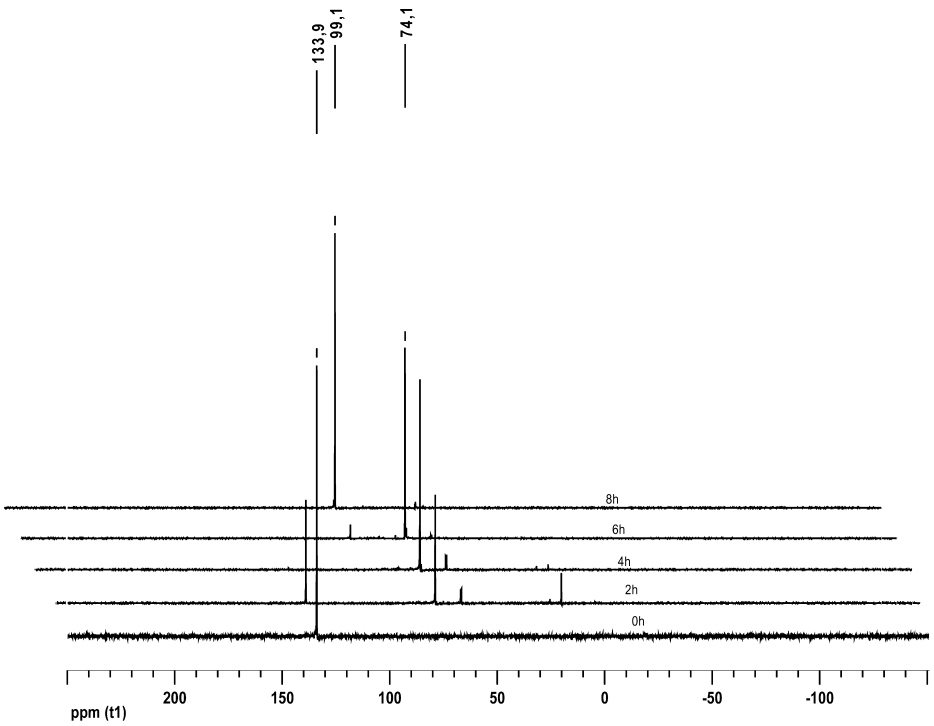
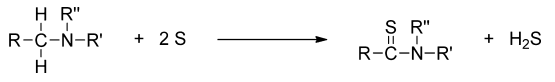


Figure 1. Progress of the conversion of **1** (0 h) over the intermediate **2** to **3a** after 2, 4, 6, and 8 h, monitored by ^{31}P NMR spectroscopy. ^{31}P NMR spectra (101 MHz) were measured in $CDCl_3$.

samples were removed from the reaction mixture after 2, 4, 6, and 8 h. In the course of the reaction, **1** (^{31}P NMR: δ ($CDCl_3$) = 134.2) is at first fully converted to **2** (^{31}P NMR: δ ($CDCl_3$) = 74.1) before the reaction proceeds to the formation of **3a** (Figure 1). In the process several intermediates are formed which are also transformed to **2** (^{31}P NMR: δ ($CDCl_3$) = 15.5, 61.9, 62.3). The starting material is consumed within 4 h of solvent reflux, but complete conversion to **2** is only achieved after about 5 h. Afterwards the formation of **3a** begins, which is completed within 8 h (^{31}P NMR: δ ($CDCl_3$) = 99.1).

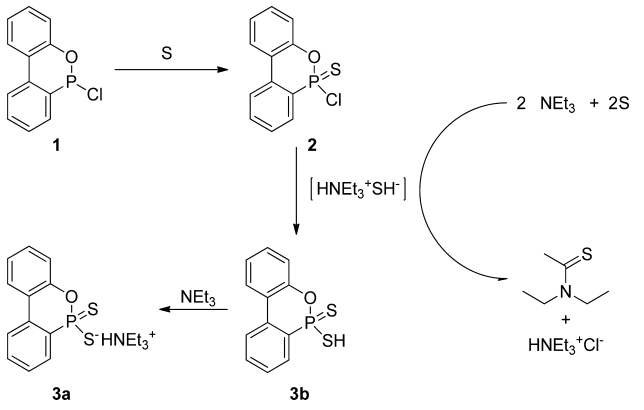
To date no detailed investigations of the mechanism of the above reaction have been carried out. However, it is likely that hydrogen sulfide is produced in situ by the reaction of triethyl amine and elemental sulfur and subsequently replaces the chloride in **2** by nucleophilic substitution. The combination of amines and sulfur as a source for hydrogen sulfide has been known for a long time.[15−17] General conversion of binary and tertiary amines with elemental sulfur to thioamides under release of hydrogen sulfide has been described (Scheme 2).[16]

Scheme 2. Formation of thioamides by reaction of sulfur in the presence of secondary or tertiary amines



The formation of ammonium hydrogen sulfide salts considered to be the major sulfuration agents in the thionation of olefins has also been reported in this context.[17] On the basis of the stoichiometry of the reaction reported here (with enough triethyl amine to intermediately catch H_2S) and the observation that no potentially evolved gas left the reaction apparatus, the formation of ammonium hydrogen sulfide can be considered a respective key step in the conversion of **2**. A proposed reaction sequence is depicted in Scheme 3:

Scheme 3. Proposed reaction scheme for the conversion of 1 to 2 in the presence of sulfur and triethyl amine



From the NMR-data provided in Figure 1, the initial conversion of **1** to **2** is verified. The proposed conversions of **2** to **3b** and of triethylamine to the thioamide via the intermediate triethylammonium hydrogen sulfide were derived from reactions that are described in the cited literature. While these are in line with the here reported conditions and observations, the occurrence has not yet been validated by experimental proof.

Synthesis of Triethyl Ammonium Diphenylphosphinodithioate (6a) and Diphenylphosphinodithioic Acid (6b). At present, the Friedel−Crafts approach is still the most widely used method for the preparation of **6b** (Scheme 4).[12] This reliable synthesis can be conducted on a laboratory scale with good reproducibility. However, it has several drawbacks since it requires an 8-fold (!) molar excess of $AlCl_3$ and two recrystallization steps to afford DPPA in a moderate overall yield of 54%. In addition to the huge synthetic effort of this reaction, the large amount of nonbiodegradeable waste

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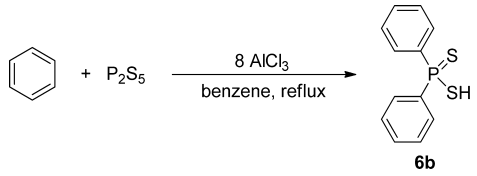
Scheme 4. Traditional synthesis of DPPA

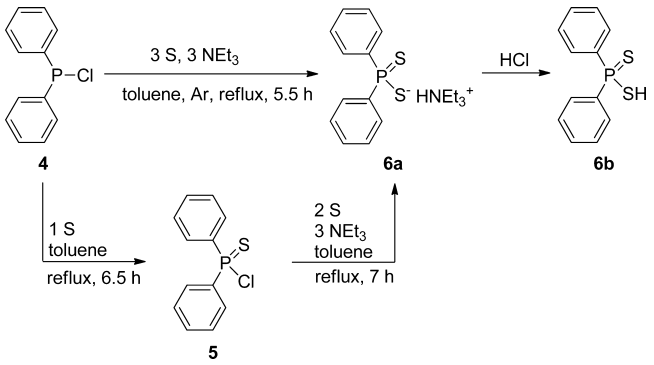


produced is a drawback that prevents this reaction from application on an industrial scale.

In an earlier approach a Grignard reagent and phosphorous pentasulfide were employed, but the product was achieved in only 24% yield.[18] An obvious approach through the sulfidation of diphenylphosphine has been published.[19] Better yields than those previously reported are available via this method (91% crude green oil compared to 80% before recrystallization). This amount is reduced by recrystallization steps to obtain the pure white and crystalline acid **6b**. However, the applicability of this reaction is primarily less attractive due to the high price of diphenylphosphine.

The lack of a convenient and easily scalable synthesis for **6a** and **6b** prompted a renewed effort in this area. Similar to the synthesis of **3a** the triethyl ammonium salt of DPPA (**6a**) can be obtained by the reaction of **4** with 3 equiv of elemental sulfur and 3 equiv of triethyl amine (Scheme 5). This

Scheme 5. Synthesis of compounds 6a and 6b: two-step and one-pot reaction pathway

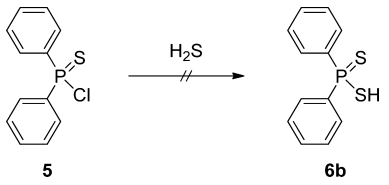


represents a new high-yielding route to the ammonia salt, **6a**, and to the free dithiophosphinic acid, **6b**, respectively, after further conversion by treatment with hydrochloric acid.

Apart from small changes in the reaction times, reaction conditions were the same as for the synthesis of **3a**. Again, it is possible to carry out the reaction in one or two steps, whereas the one-pot reaction is significantly advantageous regarding effort and reaction time. Yields are between 62% and 69% for the pure white crystalline **6a**. Yet, the crude salt can be obtained as a brownish crystalline solid in a yield of 96% and a purity of >99% (determined by ^{31}P NMR spectroscopy), which is sufficient for most of the following chemistry. From the crude **6a** the free acid **6b** can be released with hydrochloric acid and isolated (crude 95%, 79% after recrystallization) or used for further reactions without isolation. The reaction was conducted on different scales, the largest of them in a 10-L reactor, starting from 3 mol of **5**. In this case, **5** was obtained by direct conversion of **4** with sulfur in a solvent-free reaction (see Experimental Section). As the yield of **5** by this pathway was 100%, both steps can also be easily combined to a one-pot reaction. To this point, the scale-up was accomplished without any drawbacks compared to a smaller scale. Therefore, the reaction may be deemed applicable for further industrial employment.

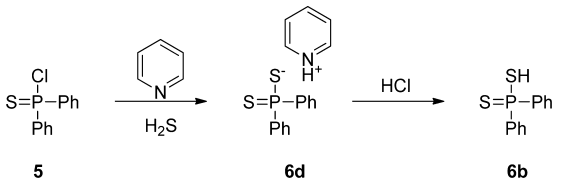
While the triethyl ammonium salt can be obtained in high yield and is often adequate for subsequent chemistry, the release and isolation of the free acid **6b** goes along with a decrease in yield. Further on, there is still room for improvement of atom efficiency for this reaction route. Therefore, a second new route to **6b** was explored. A first approach was the direct conversion of **5** to **6b** by treatment with hydrogen sulfide (Scheme 6).

Scheme 6. Direct conversion of 5 to 6b by treatment with hydrogen sulfide



However, in toluene at atmospheric pressure and room temperature, no conversion was obtained. Even when stoichiometric amounts of pyridine were added, no reaction occurred. High yields were achieved when pyridine was applied as solvent (Scheme 7).

Scheme 7. Reaction scheme for the conversion of 5 to 6d by treatment with hydrogen sulfide in pyridine; 6b can be obtained from 6d in a separate reaction step



The conversion of **5** to **6d** under these conditions is fast and nearly quantitative. The reaction mixture was then concentrated by solvent evaporation under reduced pressure and diluted with water and aqueous hydrochloric acid solution, and the product **6b** was extracted with MTBE in high yield (95%) and good purity (98%, determined by ^{31}P NMR). While this route represents a scalable and reproducible process, the direct conversion of **5** to **6b** was not feasible. The large amount of hydrochloric acid needed for the neutralization of **6d** and remaining excess pyridine is a drawback for this synthetic route. Toxicity and limitation in transportation of hydrogen sulfide reflect further disadvantages of the applicability of this process. Since the synthesis of **6b** in just one reaction step failed, the next approach was the use of sodium hydrogen sulfide as reagent for the conversion of **5** to **6b**.

Remarkably, simple treatment of **5** with technical grade sodium hydrogen sulfide, utilizing water as a reaction solvent affords sodium dithiodiphenylphosphinate (**6c**) in nearly quantitative yield (Scheme 8). Subsequent acidification with hydrochloric acid readily affords **6b** in very high yield (>98%) and with excellent purity. The acidification starting from the sodium salt **6c** proceeds more smoothly compared to the same reaction starting from the triethyl ammonium salt **6a**. This synthetic access to **6b** is superior to all other routes reported.

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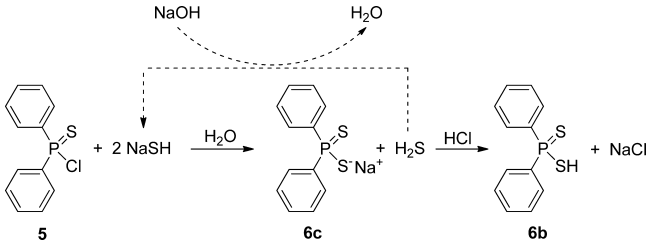
Scheme 8. Synthesis of 6b via treatment of 5 with sodium hydrogen sulfide



Scale-up was successfully carried out in a 10-L reactor, the largest batch starting from 6.5 mol of **5**. Since no decreases in yield or purity were observed, the reaction seems to be well-suited for industrial employment. The evolved H_2S is easily absorbed by sodium hydroxide to form sodium hydrogen sulfide which can be reused in this process. Thus, the necessity for disposal of H_2S can be avoided which further enhances the efficiency of the process.

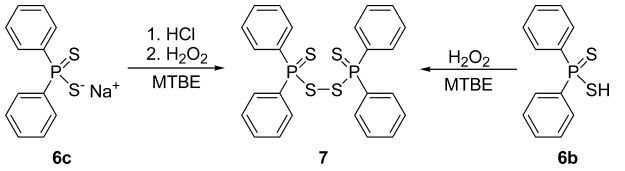
Synthesis of Bis(diphenylphosphinothioyl) Disulfide. Good availability of dithiophosphinic acids **3** and **6** as starting materials enables a broad variety of subsequent reactions. Recently, the *Michael*-like addition of **3a** to different acrylates as well as benzoquinone was reported.[14] Also the preparation of bis(diphenylphosphinothioyl) disulfide has been investigated, and different synthetic approaches have been reported.[20−23]

However, none of the known procedures is suitable for scale-up or industrial application as noted in Table 1. In an earlier approach, the expensive trichloroacetonitrile was applied as oxidation agent, leading to an overall yield of only 49%.[21] Even lower yields (40%) were achieved in a more cumbersome synthesis in which **6b** was allowed to react with tetrachloromethane and sodium ethanolate to form **7**.[23] A feasible lab-scale synthesis has been developed in which **6c** is converted to **7** in high yield (92%) by treatment with iodine/potassium iodide.[22] While this synthesis works well on a laboratory scale, an industrial application is not feasible because of the high price of iodine. A feasible and scalable synthesis of diphenylphosphinothioyl disulfide (**7**) has now been developed (Scheme 9).

Table 1. Comparison of different synthetic pathways to 6b

advantages	drawbacks
Grignard Reaction	
–	low yield (24%)
	expensive, high effort
Electrophilic Substitution (Friedel−Crafts Reaction)	
large-scale published	moderate yield (54%)
	8-fold molar excess of $AlCl_3$
	poor atom economy, large amount of waste, high effort
Sulfidation of Ph_2H	
one-pot reaction	high price of Ph_2PH
crude yield: 91% (compared to 80% for earlier approaches)	handling of Ph_2PH
Treatment of 4 with S_8 and NEt_3	
inexpensive reactants, small effort	additional step necessary for the release of **6b**
high crude yield of **6a** (96%), 99% purity	
acidification affords 79% pure **6b** (95% crude)	
Treatment of 5 with H_2S	
very high yield (95%)	additional step necessary for the release of **6b**
no further purification necessary	H_2S handling and availability
Treatment of 5 with NaSH	
pure **6b** is easily accessible in a one-pot reaction in very high yield (>98%) and purity	H_2S evolution
H_2O as solvent, inexpensive reactants	
possible recycling of H_2S, NaCl as sole byproduct	

Scheme 9. Preparation of 7 starting from the sodium salt 6c or from the free acid 6b



7 is accessible from free acid **6b** via simple oxidation with H_2O_2 in methyl-*tert*-butyl ether (MTBE) in nearly quantitative yield (99.7%, purity 99% determined by ^{31}P NMR). It is noteworthy that no elaborate workup is required. The product **7** precipitates from the reaction mixture and is obtained in excellent purity after collection by filtration and washing with MTBE and water. The acid **6b** can also be released in situ from the sodium salt **6c** by treatment with hydrochloric acid solution. In this case, the purity and yield of the product are slightly lower (yield 98.8%, purity >98% determined by ^{31}P NMR). Both routes are easy to scale up. Therefore, no obstacles are left for an industrial application of this process.

CONCLUSION

A novel route to **3a** and **6a** (and **3b** and **6b**, respectively) has been established. With the employment of very inexpensive, readily available elemental sulfur and triethylamine as starting materials, this represents a high-yielding, one-pot synthesis which is easy to scale up and is therefore suitable for industrial application. This method is superior to the routes that have been previously reported. A second development is even more remarkable. The conversion of **5** to **6c** by treatment with inexpensive technical grade sodium hydrogen sulfide in water as a solvent and subsequent acidification with hydrochloric acid proceeds smoothly and rapidly to produce diphenylphosphinothioic acid (**6b**) in excellent yield and purity. Scale-up was successfully carried out (3 mol scale). On an industrial scale, the evolved H_2S is easily recyclable in the form of sodium hydrogen sulfide, which leads to sodium chloride as the sole byproduct of this reaction and results in a very high atom efficiency and low overall cost of the process. In a subsequent reaction the disulfide **7** was synthesized by simple oxidation of **6b** with hydrogen peroxide, using MTBE as a solvent. Since **7** precipitates from the reaction mixture in excellent yield and purity, workup is quite simple. Again this reaction is superior to known procedures.

EXPERIMENTAL SECTION

General Experimental. Unless stated otherwise, all reactants and solvents were purchased from commercial sources and used without further purification or drying. **1** was synthesized according to previously reported procedures.[24] Standard glass apparatus was used; reactions were carried out with magnetic stirring and, if moisture sensitive, in flame-dried glassware under argon. For reactions that were conducted in a

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reactor, the following reactor components were used: (i) 10-L reactor, equipped with a three-step cross-beam agitator and baffle, condenser, and dropping funnel; (ii) thermostat for the thermoregulation of the reactor jacket; (iii) pump and controller for the dosage of the feed; (iv) flexible-tube pump for the dosage of MTBE and HCl solution; (v) alkaline scrubbing tower (hold-up 4 L, 15% NaOH solution) for flue gas scrubbing; (vi) H_2S-monitoring by an H_2S sensor in the hood.

NMR spectra were obtained at room temperature. Chemical shifts are reported as δ values relative to the solvent absorption. All ^{31}P NMR spectra were obtained with proton decoupling. All ^{13}C NMR spectra were obtained with proton decoupling and phosphorus coupling. ^{1}H NMR spectra were obtained with phosphorus coupling. Melting points are uncorrected. High-resolution mass spectrometry (HR-MS) analyses were performed using electron ionization (EI, 70 eV) or electrospray ionization (ESI) and time-of-flight (TOF) analyzers.

Synthesis of Triethylammonium 6*H*-Dibenzo[*c*,*e*][1,2]-oxaphosphinine-6-thiolate 6-Sulfide (3a). **1** (65.73 g, 280 mmol) was charged to a three-necked, round-bottomed flask equipped with condenser, thermometer, magnetic stirrer bar, and argon inlet and dissolved in anhydrous toluene (300 mL) at room temperature. Elemental sulfur (26.95 g, 840 mmol) and triethylamine (85.05 g, 840 mmol) were added, and the reaction mixture was heated to solvent reflux temperature and kept there for 8 h. During this time, a dark-brown suspension developed. Samples for ^{31}P NMR analysis were removed after 2, 4, 6, and 8 h. After 6 h **1** was fully consumed, and the intermediate **2** was exclusively formed (δ ($CDCl_3$) = 74.5). After 8 h complete conversion to the target product was achieved (δ ($CDCl_3$) = 99.2). The reaction mixture was then cooled to 0 °C in an ice bath and filtered. The precipitate was washed with cold toluene and cold water and dried at reduced pressure to yield the target compound as a brownish crystalline solid (89.37 g, 87%). Mp 128−130 °C; ^{31}P NMR: δ ($CDCl_3$) = 99.2; ^{1}H NMR: δ ($CDCl_3$) = 1.36 (t, J = 7.3 Hz, 9H), 3.22 (m, 6H), 7.11−7.19 (m, 2H), 7.27−7.32 (m, 1H), 7.38−7.47 (m, 2H), 7.72−7.77 (m, 1H), 7.83−7.86 (m, 1H), 8.07 (dd, J = 15.5 Hz, J = 7.0 Hz, 1H), 9.69 (s, 1H); ^{13}C NMR: δ ($CDCl_3$) = 8.5 (s, 3C), 46.0 (s, 3C), 120.7 (d, J_{PC} = 5.3 Hz, 1C), 123.2 (s, 1C), 123.4 (s, 1C), 124.6 (d, J_{PC} = 12.8 Hz, 1C), 124.9 (d, J_{PC} = 1.4 Hz, 1C), 127.9 (d, J_{PC} = 14.6 Hz, 1C), 128.3 (d, J_{PC} = 13.8 Hz, 1C), 129.3 (s, 1C), 130.1 (d, J_{PC} = 2.7 Hz, 1C), 132.1 (d, J_{PC} = 5.5 Hz, 138.7 (d, J_{PC} = 103.4 Hz, 1C), 150.9 (d, J_{PC} = 10.3 Hz, 1C), HR-EI calcd ($C_{12}H_9OS_2P$) m/z = 263.9832, found m/z = 263.9836.

Synthesis of Triethyl Ammonium Diphenylphosphinodithioate (6a). *A. Two-Step Reaction via **5**.* Under an inert atmosphere, elemental sulfur (90.1 g, 0.35 mol) was added to **4** (620.8 g, 2.81 mol) and heated to 130 °C. At this temperature, the reaction mixture was stirred for 6.5 h and then allowed to cool to room temperature. **5** was obtained as clear yellowish oil (713 g, 100%). The product was used for the next step without further purification. ^{31}P NMR: δ ($CDCl_3$) = 81.6; ^{1}H NMR: δ ($CDCl_3$) = 7.39−7.52 (m, 6 H), 7.93−8.03 (dd, J = 15.6 Hz, J = 7.9 Hz, 4H); ^{13}C NMR: δ ($CDCl_3$) = 128.6 (d, J_{PC} = 14.6 Hz, 4C), 130.9 (d, J_{PC} = 12.6 Hz, 4C), 132.6 (d, J_{PC} = 3.4 Hz, 2C), 135.3 (d, J_{PC} = 96.4 Hz, 2C); HR-EI: calcd ($C_{12}H_{10}ClPS$) m/z = 251.9929, found m/z = 251.9941.

In the next step, toluene (2.4 L), elemental sulfur (192.3 g, 6.1 mol), and **5** (757.5 g, 3.0 mol) were placed in a 10-L reactor at room temperature. The reaction mixture was warmed up to 60 °C, and triethylamine (934 g, 9.25 mol) was added within 20 min. The reaction mixture was heated to reflux and stirred at reflux temperature for 6 h. The reaction mixture was then cooled down to rt, and water (5 L) was added while stirring. The resulting suspension was stirred for 1 h at ambient temperature. The precipitate was isolated via suction filtration and subsequently washed with cold water (1 L) and cold toluene (1 L). The crystals were collected and dried in a vacuum oven (T = 60 °C) overnight to afford the crude product as a brownish crystalline solid (1012 g, 96%). The crude product was divided into two batches of 506 g each and batchwise purified via recrystallization from hot water (14 mL water/g) and charcoal (150 mg charcoal/g). The product crystallized as white crystals. The two batches were combined to afford 725 g (69%) of triethyl ammonium dithiodiphenylphosphinate.

B. One-Pot Reaction. In a three-necked, round-bottomed flask equipped with a condenser, thermometer, and argon inlet, was dissolved **4** (20 g, 90.65 mmol) in 120 mL of dry toluene. Elemental sulfur (8.72 g, 272 mmol) and triethylamine (27.52 g, 272 mmol) were added, and the reaction mixture was then heated at solvent reflux temperature for 5.5 h. During this time a precipitate formed, and the color changed from light yellow to dark brown. Afterwards, the suspension was cooled to 0 °C in an ice bath, and triethylammonium chloride was removed by filtration. From the filtrate, the product crystallized overnight. The crystals were collected by filtration at reduced pressure and washed with cold toluene and cold water. Recrystallization (see above) yielded 19.3 g (62%) of white crystals. Note: instead of letting the product crystallize from the mother liquor, the same workup as in A may be chosen, to yield 96% of crude or 69% of the pure **6a**. Mp 109 °C; ^{31}P NMR: δ ($CDCl_3$) = 62.6; ^{1}H NMR: δ ($CDCl_3$) = 1.29 (t, ^{3}J = 7.3 Hz, 9H), 3.22 (m, 6H), 7.26−7.33 (m, 6H), 8.12 (dd, J = 13.8 Hz, J = 6.0 Hz, 4H), 10.17 (s, 1H); ^{13}C NMR: δ ($CDCl_3$) = 8.3 (s, 3C), 45.7 (s, 3C), 127.4 (d, J_{PC} = 12.6 Hz, 4C), 129.0 (d, J_{PC} = 3 Hz, 2C), 130.4 (d, J_{PC} = 11.4 Hz, 4C), 143.4 (d, J_{PC} = 80.3 Hz, 2C); Anal. Calcd for $C_{18}H_{26}NPS_2$: C 61.5, H 7.4, N 4.0, S 18.2, P 8.8; found C 60.8, H 7.5, N 3.9, S 17.9, P 8.5. HR-EI: calcd ($C_{12}H_{10}PS_2$): m/z = 248.9957, found: m/z = 248.9962.

Synthesis of Diphenylphosphinodithioic Acid (6b). *A. Conversion of **6a** with Hydrochloric Acid.* In a round-bottomed flask equipped with a condenser was dissolved the crude **6a** (8.4 g, 23.9 mmol) in ethanol (40 mL) at 80 °C. At this temperature concentrated aqueous hydrochloric acid solution (50 mL) was added. A brownish solid precipitated, and the resulting suspension was stirred for 5 min. Brine was added (50 mL), and the reaction mixture was cooled to 5 °C in an ice bath. It was filtered, and the residue was washed with cold water and dried at reduced pressure to yield 5.7 g of the crude acid **6b** (95%) as a brownish solid. The purity of the crude product was already at 99% as determined by ^{31}P NMR spectroscopy. Recrystallization from isopropanol yielded 4.7 g (79%) of the pure compound as white crystals.

*B. Via Conversion of **5** with Hydrogen Sulfide.* A 750-mL glass reactor equipped with stirrer, thermometer, gas-inlet tube, gas-outlet, and bubble counter was coupled to a weighted H_2S-bottle and an argon purging line via a security bottle. The gas-outlet was coupled to a wash tower filled with 10% aqueous NaOH solution. In the glass reactor, **5** (75 g, 0.3 mol) was dissolved in pyridine (300 mL) at room temperature, forming a clear yellowish solution in a slightly exothermic reaction. The reaction mixture was heated to 30 °C, and H_2S (20.7 g, 0.6

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mol) was bubbled into the solution (beneath the surface) within 45 min. During this process, the temperature rose to 40 °C until 1 equiv of H_2S had been added, and then the temperature fell. The apparatus was purged with argon, and the reaction mixture was heated to 40 °C and stirred for 1 h at this temperature. Then two-thirds of the pyridine (200 mL) was removed by evaporation at reduced pressure, and MTBE (270 mL) was added to the viscous residue. An aqueous solution (37%) of hydrochloric acid (150 g, 1.52 mol) was poured into the suspension to dissolve the solid ingredients, thereby forming an emulsion. This emulsion was stirred for 1 h, after which the phases were separated. Evaporation of the organic phase yielded **6b** as a brittle yellow solid (70.6 g, 95%).

*C. Via Conversion of **5** with Sodium Hydrogen Sulfide.* In a 10-L reactor, a suspension of sodium hydrogen sulfide (962 g, 13.0 mol) in 2 L of water was heated to 95 °C. When this temperature was reached, the salt was completely dissolved and chlorodiphenylphosphine sulfide (1642 g, 6.5 mol) was added within 1 h via a ProMinent-Pump. After a retardation period, H_2S-evolution started and continued until the addition was completed. Afterwards, the reaction mixture was stirred for 1 additional hour at 95 °C. With the addition of ice (500 g) the solution was then cooled to 50 °C. At this temperature, MTBE (2.5 L) was poured into the reactor via a flexible-tube pump over a period of 15 min. The reaction mixture was cooled to 25 °C, and 15% hydrochloric acid solution (1581.7 g, 6.5 mol) was added via flexible-tube pump. After another 30 min of stirring at room temperature, the phases were separated, and the organic phase (MTBE) was cooled to 2 °C in an ice bath while stirring. In the process, the diphenylphosphinedithioic acid crystallized. After 1 additional hour of stirring, the crystals were collected via filtration at reduced pressure and afterwards dried in an oven at reduced pressure to afford 1073 g (93%) of a white crystalline solid. Mp 58 °C; ^{31}P NMR: δ ($CDCl_3$) = 56.6; ^{1}H NMR: δ ($CDCl_3$) = 2.88 (s, 1H), 7.43−7.55 (m, 6H), 7.91−8.01 (dd, J = 15.0 Hz, J = 8.1 Hz, 4H); ^{13}C NMR: δ ($CDCl_3$) = 128.5 (d, J_{PC} = 13.7 Hz, 4C), 130.9 (d, J_{PC} = 11.9 Hz, 4C), 131.9 (d, J_{PC} = 3.3 Hz, 2C), 135.4 (d, J_{PC} = 85.8 Hz, 2C); Anal. Calcd for $C_{12}H_{11}PS_2$: C 57.6, H 4.4, S 25.6, P 12.4; found C 57.1, H 4.4, S 25.4, P 12.1; HR-EI: calcd ($C_{12}H_{11}PS_2$) m/z = 250.0040, found m/z = 250.0036.

Synthesis of Bis(diphenylphosphinothioyl) Disulfide (7). In a three-necked, round-bottomed flask equipped with a condenser, thermometer, dropping funnel and argon inlet, **6b** (325.4 g, 1.3 mol) was dissolved in MTBE (2.5 L) and cooled to 2−5 °C in an ice bath. At this temperature aqueous hydrogen peroxide (73.6 g, 0.64 mol) was dropped into the reaction mixture over a period of 15 min. During this time a white solid precipitated. The newly formed suspension was stirred for one hour at 5 °C and then filtered. The residue was washed with a small amount of MTBE and subsequently dried at reduced pressure at 50 °C, to yield 323.1 g (99.7%) of a white crystalline solid. Mp 145 °C ^{31}P NMR: δ ($CDCl_3$) = 69.5; ^{1}H NMR: δ ($CDCl_3$) = 7.32−7.48 (m, 12H), 7.76−7.85 (dd, J = 14.3 Hz, J = 7.0 Hz, 8H); ^{13}C NMR: δ ($CDCl_3$) = 128.4 (d, J_{PC} = 13.8 Hz, 4C), 131.9 (d, J_{PC} = 11.6 Hz, 4C), 132.2 (d, J_{PC} = 3.1 Hz, 2C), 132.8 (d, J_{PC} = 70.0 Hz, 2C). HR-EI: calcd ($C_{24}H_{20}P_2S_4$) m/z = 497.9923, found m/z = 497.9968.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H, ^{13}C, and ^{31}P NMR spectra of all the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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