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Transfer of Sulfur from Arsenic and Antimony Sulfides to Phosphorus Sulfides. Rational Syntheses of Several Less-Common P_4S_n Species

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It has been shown that triphenylarsenic sulfide and triphenylantimony sulfide rapidly transfer sulfur to a number of the known phosphorus sulfides. The reactions are performed at or below room temperature in carbon disulfide solutions. The transfers are neither highly selective nor random, making them useful but not ideal for synthetic purposes. The moderate selectivities of the reactions have been used in the assignment of structures to two new phosphorus sulfides, structures with molecular formulas P_4S_6 and P_4S_8. The reactions of P_4S_3 are unusual in that products with 7−9 sulfur atoms in the molecule are formed competitively with low sulfur products. The usefulness of triphenylantimony sulfide is limited by its tendency to undergo reductive elimination of sulfur. This reduction takes the form of a disproportionation to give triphenylantimony and elemental sulfur and has been shown to occur by a second-order process that appears to involve the formation of disulfur, S_2.

Introduction

The preceding paper[1] discusses the reactions of elemental phosphorus with elemental sulfur. In the history of this chemistry, there have been relatively few tools in the craft of assembling the products of these reactions. In fact, all synthetic efforts can be collected into three categories: thermal reactions (t),[2−7] abstraction of sulfur with phosphines (a),[8−10] and construction of P−S bonds with sulfur equivalents (c).[11−13] Examples of these three types of reaction are shown in Figure 1. An association can be made between each of the previously isolated phosphorus sulfides and its methods of preparation, as is done in Figure 2. Clearly, the most common method is the equilibration of a mixture of phosphorus, or alternatively a lower sulfide, and sulfur.

The nonthermal reactions in Figure 1 are mild and reasonably specific. Triphenylphosphine apparently plucks off an exocyclic sulfur from the outside of a phosphorus sulfide cage in distinct preference to removal of an endocyclic sulfur. The oxidation reactions shown in Figure 1 are quite specific: the intermediate diiodide (or similar structure) is required in order to carry out the second step. It is evident there are few known ways in which this class of compounds can be intelligently manipulated.

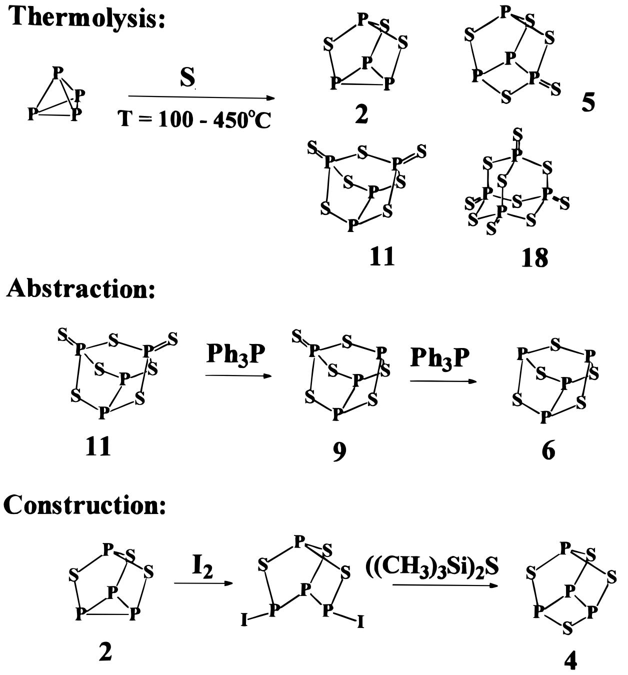

Figure 1. Examples of the known synthetic methods used to prepare phosphorus sulfides.

It was in asking the question whether the reduction of phosphorus sulfides with triphenylphosphine was a reversible reaction that another tool in the synthetic chemistry of these compounds was struck. Triphenylphosphine sulfide, under any reasonable conditions, does not return sulfur to any of the easily prepared phosphorus sulfides. But Baechler had already shown that other, better, sulfur donors exist and that the rates of sulfur transfer from triphenylarsenic sulfide or triphenylantimony sulfide to triphenylphosphine were fast.[14] It remained only to put the phosphorus sulfides together with these more willing donors.

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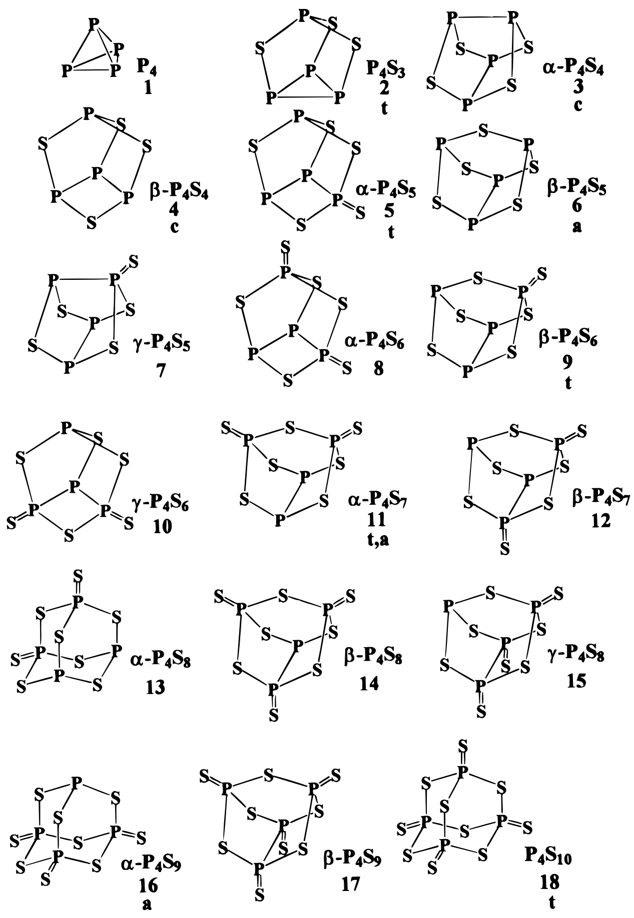

Figure 2. Known phosphorus sulfides, their trivial names, and the literature methods used to prepare them. In the figure "t" refers to thermal, "a" to abstraction, and "c" to construction methods of synthesis. See text for discussion.

The reactions of phosphorus sulfides with triphenylarsenic sulfide and triphenylantimony sulfide have provided the synthetic entry into heretofore unavailable phosphorus sulfides as well as deliver strong evidence for the structures of several phosphorus sulfides that have only been observed as low concentration products from the reactions of phosphorus and sulfur. These reactive triphenylelement sulfides have the potential to be remarkable reagents for both the transfer of sulfur, to phosphorus and other acceptors, and the determination of sulfide structures.

Experimental Section

General Information. P_4S_3 was obtained from Fluka Chemical Co. It was recrystallized from CS_2 prior to use. P_4S_{10} was purified by Soxhlet extraction. Carbon disulfide used for spectroscopy was used as received (Fisher); the carbon disulfide used as solvent for chemical reactions was dried by refluxing over P_4S_{10}. α-P_4S_5,[15] β-P_4S_5,[4] α-P_4S_7,[5] and α-P_4S_9[3] were prepared according to literature procedures. Triphenylphosphine, triphenylarsenic, and triphenylantimony are commercially available from Aldrich Chemical Co., and triphenylantimony sulfide is available from Strem Chemical Co. Only triphenylphosphine was recrystallized (EtOH) prior to use. Triphenylphosphine sulfide was harvested from the preparation of β-P_4S_5 and recrystallized twice. Triphenylarsenic sulfide was prepared according to the literature.[14]

All of the synthetic and sample preparations were performed either using Schlenk techniques, under nitrogen, or in a glovebag. Sulfides were most commonly stored under vacuum in Schlenk tubes in the dark. Spectroscopy was performed as described in the previous paper.[1]

Spin simulation and refinement calculations were performed using the program gNMR (Cherwell, Ltd., available from SoftShell). All of the chemical shifts and coupling constants for the species reported in this study were obtained by fitting the spectroscopic data. A table of these data can be found in the Supporting Information.

Typical Reaction of Triphenylarsenic or Triphenylantimony Sulfide with a Phosphorus Sulfide. A 100 mL three neck flask, fitted with a reflux condenser, nitrogen inlet, thermocouple, and magnetic stirring bar, was charged, in order, with 30 mL of dry carbon disulfide, 0.185 g (5.3×10^{-4} mol) of α-P_4S_7, and 0.539 g (15.9×10^{-4} mol) of triphenylarsenic sulfide, all at room temperature. A thin slurry of α-P_4S_7 was produced. At 30 min, the solution had become cloudy. After 2 h, an off-white precipitate had formed and the solution was no longer cloudy. The newly formed precipitate had deposited on the unreacted α-P_4S_7. Samples of the carbon disulfide layer were removed, added to a nitrogen-purged NMR tube containing a lock capillary, and analyzed by ^{31}P NMR spectroscopy.

Synthesis of α-P_4S_6. To a Schlenk flask was added 0.224 g (7.88×10^{-4} mol) of α-P_4S_5 and 90 mL of dry carbon disulfide. Triphenylarsenic sulfide, 0.265 g (7.84×10^{-4} mol), was added as a dry solid under nitrogen. After 2 h, ^1H and ^{31}P NMR spectroscopy showed greater than 90% reduction of the triphenylarsenic sulfide and slightly more than 50% conversion of the α-P_4S_5 to other products. A second addition of arsine sulfide, 0.204 g (6.02×10^{-4} mol), was made and the reaction continued at room temperature for another 2 h. The phosphorus sulfides were precipitated by the addition of 11 mL of dry toluene and removal of the carbon disulfide under mild vacuum. A light yellow solid was obtained that was filtered under argon, washed with toluene, and dried under vacuum. This solid contained a small amount of residual α-P_4S_5 along with α-P_4S_6 as the major product, γ-P_4S_6, α-P_4S_7, and a very small quantity of β-P_4S_8. Most of the α-P_4S_7 could be removed by partially dissolving the crude solids in 90 mL of hot carbon disulfide and filtering. A second crop of α-P_4S_7 was removed by cooling the filtrate in CO_2/acetone and filtering the slurry. The product was obtained by evaporating the filtrate to about 5 mL total volume under vacuum followed by filtration. The assay of this material by ^{31}P NMR showed 84% α-P_4S_6, 10% γ-P_4S_6, and 6% α-P_4S_7. This mixture gave an M + 1 peak for P_4S_6 as the base peak in the (isobutane) CI mass spectrum.

Synthesis of β-P_4S_8. α-P_4S_7, 0.142 g (4.071×10^{-4} mol), was added to 250 mL of dry, distilled carbon disulfide in a round bottom flask. The mixture was maintained under a nitrogen atmosphere and stirred until only a small amount of solid remained. A solution of 0.116 g (3.42×10^{-4} mol, 84% of theory) of triphenylarsenic sulfide in 10 mL of dry carbon disulfide was loaded into a syringe. The sulfide solution was added through a septum to the α-P_4S_7 solution in 1 mL increments over the course of 140 min. The mixture was allowed to stir overnight at room temperature. The ^{31}P NMR spectrum of the CS_2 solution showed only α-P_4S_7 and β-P_4S_8. After 24 h, 10 mL of dry toluene was added and most of the CS_2 distilled at atmospheric pressure. The precipitate that formed was identified as α-P_4S_7, and the filtrate showed a 1:3 ratio of α-P_4S_7 to β-P_4S_8. Attempts to further enrich this material in β-P_4S_8 were not successful.

Kinetics of Triphenylantimony Sulfide Decomposition. Solution kinetics were performed by diluting 84.4 mg of commercial triphenylantimony sulfide in a 10 mL volumetric flask with dry, distilled carbon disulfide. The solution concentration was 0.022 M. Four NMR tubes were prepared from this stock solution by volumetric dilution directly in the tubes. The NMR tubes were evacuated and sealed. The NMR spectrometer was thermostated at 35.0 °C. The ^1H NMR spectroscopy used a 30° pulse, a 10 s delay, and summation of 16 transients. The aromatic signals for triphenylantimony sulfide and triphenylantimony are baseline resolved, and quantitation was performed by integration of these signals. The analysis of the kinetics was performed by numerical integration using the program SIMUSOLV (Mitchell and Gauthier).

Reaction of Triphenylantimony Sulfide with 2,3-Dimethylbutadiene. To a 5 mL flask fitted with a stir bar and septum was added, in order, 0.85 g (2.21 mmol) of triphenylantimony sulfide, 0.93 g (11.3 mmol) of 2,3-dimethylbutadiene (Aldrich), and 1 mL of f CS_2. The mixture was sealed with a septum and stirred overnight at room temperature. After about 18 h, the material was a paste, primarily as a result of loss of CS_2 by evaporation. A small sample of the reaction mass was dissolved in CS_2 in an NMR tube. The ^{13}C NMR peaks for

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(15) Brauer, G. *Handbook of Preparative Inorganic Chemistry*; Ferdinand Enke Verlak: Stuttgart, Germany, 1960; p 506.

Table 1. Reactant Ratios and Products from the Reactions of Phosphorus Sulfides with Triphenylarsenic Sulfide (**19**) and Triphenylantimony Sulfide (**21**)

reacn no.	sulfide	Ph_3MS	Ph_3MS/ P_4Sn	product composn																
				2	**3**	**5**	**6**	**8**	**9**	**10**	**11**	**12**	**14**	**15**	**16**	**17**	**18**	**E**	**F**	**H**
1	P_4S_3 (**2**)	**19**	1.2	93							1		1		3		2			
2	P_4S_3 (**2**)	**21**	0.7	95				0.5			1		0.5		3	*a*	1			
3	α-P_4S_5 (**5**)	**19**	0.2	2		76		14		6	2									
4	α-P_4S_5 (**5**)	**19**	1.0	1		46		33		9	11									
5	α-P_4S_5 (**5**)	**19**	2.0	2		0		47			25		5		21					
6	α-P_4S_5 (**5**)	**19**	1.0	1		18		61		13	6		1							
7	α-P_4S_5 (**5**)	**19**	1.0			39		37		21	4		*a*							
8	*β*-P_4S_5 (**6**)	**19**	0.9				42		35		15	7								
9	*β*-P_4S_5 (**6**)	**19**	4.5								30		70				1			
10	α-P_4S_7 (**11**)	**19**	0.6								28		69				1	1		
11	α-P_4S_7 (**11**)	**19**	1.0								28		67	*a*			*a*	4		
12	α-P_4S_7 (**11**)	**19**	2.0								20		73	1			1	5		
13	α-P_4S_7 (**11**)	**21**	1.7								29		20		37	*b*	14		*b*	*b*
14	α-P_4S_7 (**11**)	**21**	3.0								15		11		54	*b*	20		*b*	*b*
15	α-P_4S_7 (**11**)	**19**	3.0								9		10		36	12	26		7	1
16	α-P_4S_7 (**11**)	**21**	4.0								0		0		31	6	63			
18	α-P_4S_9 (**16**)	**19**	0.5								4		5		53		39			
17	α-P_4S_9 (**16**)	**19**	2.0												58		42			
19	P_4S_{10} (**18**)	**19**	1.0												0		100			

[a] Visible by NMR spectroscopy but too small to quantify. [b] Appears in filtrate after filtration and standing at room temperature for 1 day.

the adduct disulfide and tetrasulfide were observed as minor components.[16] These results are discussed below.

Results

Reactions of Phosphorus Sulfides with Triphenylarsenic Sulfide (19). The relative concentrations of the products of many of the reactions performed in this study are collected in Table 1. The relative percent figures in Table 1 are taken from the ^{31}P NMR spectra of the CS_2-soluble material from the reaction and therefore are not relative *yields*. The data in Table 1 should be used to separate major from minor products. Because of the small scale (1−5 mg) of many of these experiments that were performed directly in NMR tubes, it was not possible to quantitatively recover and independently assay the solids. The structures of the products, as well as they are understood, are shown in Figure 2. The structures for compounds E, F, and H are unknown at this time, though the chemical shifts and coupling constants have been refined. Compound E shows two triplets: 92.3 and 39.2 ppm with a coupling constant of 12.3 Hz. Compound F shows three unique phosphorus signals: P_1, 47.6 ppm; $P_{2,3}$, 42.7 ppm; P_4, 26.5 ppm; coupling constants $J_{1,2-3} = 32.3$ Hz, $J_{1,4} = 29.0$ Hz, and $J_{2-3,4} = 88.8$ Hz. Compound H shows an A_3B pattern: P_1, 44.9 ppm; P_{2-4}, 27.6 ppm; $J_{1,2-4} = 29.9$ Hz. The mixtures in which these sulfides appear, the chemical shift ranges, and the small coupling constants all argue that these materials are phosphorus−sulfur cages of high sulfur content. They are produced from reactions with both triphenylarsenic sulfide and triphenylantimony sulfide, making it unlikely they incorporate the Ph_3M group in the structure.

These reactions would often not go to completion, as measured by the ^1H NMR spectrum of the solution. The chemical shifts of **19** and triphenylarsenic (**20**) are well separated and easily integrated. The higher sulfides (α-P_4S_9, P_4S_{10}) appear capable of transferring sulfur to **20**. Thus, unlike the removal of sulfur from higher sulfides with triphenylphosphine, an apparently irreversible reaction, the transfer of sulfur from **19** to phosphorus compounds is reversible.

Reactions of Phosphorus Sulfides with Triphenylantimony Sulfide (21). The work of Baechler and his students[14] predicted that triphenylantimony sulfide (**21**) would react even more efficiently than **19** with phosphorus sulfides. The equilibrium constants for transfer of sulfur to the phosphorus sulfides should then be larger than for **19**; the transfers should be more nearly quantitative. However, the reactions between the phosphorus sulfides and **21** were far less complete than with **19** at the same stoichiometry.

Attempts to prepare moderate concentration solutions of **21** in carbon disulfide resulted in disproportionation to give triphenylantimony (**22**) and a noncrystalline form of sulfur. These results are discussed below. Typically, cold carbon disulfide would be added to a flask containing **21** and the phosphorus sulfide cooled in an ice bath in order to minimize the disproportionation. The reactions were allowed to proceed cold for a few minutes and were then warmed slowly to room temperature. In all cases, a precipitate of an uncharacterized form of sulfur, often contaminated with phosphorus sulfides, was noticed immediately upon addition of the carbon disulfide. Because of these limitations on the use of **21**, most of the synthetic and mechanistic studies were performed with the arsenic sulfide **19**.

Reactions of Phosphorus Sulfides with Triphenylarsenic and Triphenylantimony. During the investigation of the possible mechanisms for these sulfide transfer reactions, it was important to know the extent to which they were reversible or participated in addition reactions with the intermediate sulfides. In separate experiments, *β*-P_4S_5 and α-P_4S_7 were allowed to react with an equivalent of **22** for 24 h in refluxing carbon disulfide. No reaction to form other phosphorus sulfides was observed by ^{31}P NMR, and no formation of triphenylantimony sulfide was observed by ^1H NMR spectroscopy.

Excess P_4S_{10} was observed to rapidly oxidize **20** to give **19**, with α-P_4S_9 as the only phosphorus sulfide produced. Similarly, α-P_4S_9 was very slowly reduced to give predominately α-P_4S_7 along with a small quantity of α-P_4S_8. Because of the slow self-reaction of **19** to give sulfur and **20**, the calculation of equilibrium constants from the data was not possible.

Stability of the Reagents. One of the first observations made in working with triphenylantimony sulfide (**21**) was its rapid reaction with itself. Although dilute solutions of this reagent could be prepared and kept for short periods of time at low temperature, high concentrations of triphenylantimony sulfide in carbon disulfide at room temperature rapidly led to the precipitation of sulfur. The reaction was observed in a number

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(16) Williams, C. R. Ph.D. Thesis, McGill University, 1991.

of common NMR solvents (CS_2, $CDCl_3$, acetone-d_6, and CD_3CN) making it unlikely the decomposition requires the participation of the solvent.

Kinetic analyses of the reduction of triphenylantimony sulfide in carbon disulfide at 35 °C were performed by ^1H NMR spectroscopy. The second-order rate constant was $0.014 \pm 0.002\ s^{-1}\ M^{-1}$. Some of the reactions displayed precise second-order kinetic behavior while others were better fit by the addition of a companion first-order process.

The self-reaction of triphenylarsenic sulfide, **19**, was significantly slower than that of the antimony sulfide. The disproportionation of **19** does not to go to completion. At 25 °C, approximately 17% of the sulfide is reduced to triphenylarsenic, **20**, as measured by ^1H NMR spectroscopy. A kinetic analysis was not performed.

Discussion

The sulfur transfer reactions of triphenylarsenic sulfide and triphenylantimony sulfide with the phosphorus sulfides have provided a much needed tool for the manipulation of these unique chemical structures. The first question evaluated was the potential of these two materials as synthetic reagents. Because of the limitations experienced with the use of **21** mentioned above, all the truly synthetic experiments were carried out with **19**. The easy syntheses of α-P_4S_5 and α-P_4S_7, as well as the importance of assigning the structures of the products expected from the single addition of sulfur to them, led to the use of these two sulfides as examples for judging synthetic utility.

From small-scale reactions it was clear the predominant product from the oxidation of α-P_4S_5 with **19** was α-P_4S_6, making it a reasonable target for isolation and purification. After removal of all of the triphenylarsenic species from the mixture, the crude mixture had the following composition: α-P_4S_5, 4%; α-P_4S_6, 71%; γ-P_4S_6, 16%; α-P_4S_7, 7%; β-P_4S_8, 1%; α-P_4S_9, 1%. A series of precipitations was used to remove all of the residual α-P_4S_5 and the two highest sulfides, β-P_4S_8 and α-P_4S_9. The analysis of the material at the end of three stages of purification was: α-P_4S_6, 84%; γ-P_4S_6, 10%; α-P_4S_7, 6%. The similar solubilities of these three prevented continued recrystallization from improving the purity of α-P_4S_6.

The stoichiometric oxidation of α-P_4S_7 with **19** gives one major product, β-P_4S_8, contaminated with unreacted starting material and small amounts of higher sulfides as shown in reaction 12 of Table 1. Attempts to purify the β-P_4S_8 by the precipitation of α-P_4S_7 led to the disproportionation of β-P_4S_8 with the formation of α-P_4S_7, both P_4S_9 isomers, P_4S_{10}, and two of the unknown sulfides, compounds F and H. This behavior is consistent with the thermal sensitivity of β-P_4S_8 discussed in the preceding article.[1]

In order for these reactions to be useful for the assignment of structure, the first formed products must be predictable from the structure of the starting phosphorus sulfide. There are a number of potential reactions that are easily drawn for these additions. The most likely are shown in Figure 3. Reactions *a* and *b* simply transfer a sulfur from arsenic to phosphorus, though the paths are quite different. Either reaction running in reverse could represent the reduction of phosphorus sulfides by triphenylphosphine, and it would be reasonable to expect that oxidation and reduction reactions are mechanistically connected. Unfortunately, there has been neither experimental nor theoretical evaluation of the mechanism of either the oxidation or the reduction reaction.

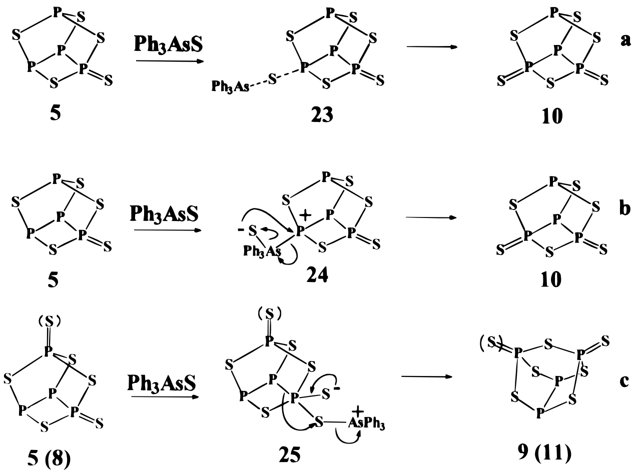

Figure 3. Examples of reaction paths for the addition of sulfur to α-P_4S_5 and α-P_4S_6.

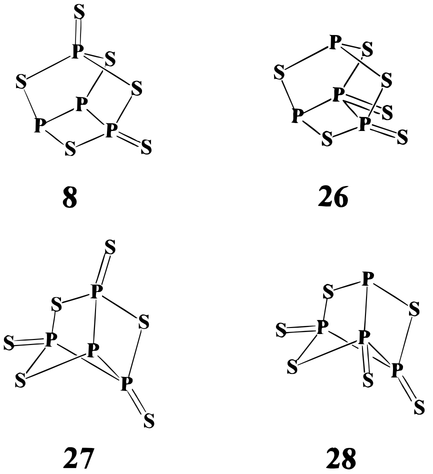

Figure 4. The four C_1 isomers of P_4S_6.

Both types of reactions shown in Figure 3, oxidation of a trivalent phosphorus and ring expansion by attack at a tetravalent phosphorus, are observed in the reactions of **19** and **21** with the various phosphorus sulfides. The reaction of α-P_4S_5 with less than 1 equiv of **19** (experiment 3, Table 1) gives rise to two major products, α-P_4S_6 and γ-P_4S_6. In *no* reaction of α-P_4S_5 with **19**, regardless of stoichiometry or reaction conditions, is β-P_4S_6 observed. Since the structures of α-P_4S_5 and β-P_4S_6 are known from X-ray diffraction studies, path *c* of Figure 3 plays no part in the reaction of α-P_4S_5 with **19**.

The work of Bjorholm has shown the mother−daughter relationship between α-P_4S_5 and α-P_4S_6, although the exact placement of the extra sulfur atom in α-P_4S_6 was left in doubt. The symmetry of α-P_4S_6 is known to be C_1. Among all of the structural isomers of P_4S_6 built upon the expansion of a P_4 tetrahedron, there are four with C_1 symmetry (Figure 4). Structures **8** and **26** are the two structures already proposed for α-P_4S_6;[6,7] structures **27** and **28** are far less likely. These last two structures utilize a phosphorus−sulfur cage that is not seen in any other known phosphorus sulfide. In addition, all *three* of the $^1J_{PP}$ values that one would measure in **27** and **28** would be large (>150 Hz), rather than only *two*.[1] Finally, one can use a plausibility argument to reinforce the distinction. The reaction of α-P_4S_5 with **19** to give either **27** or **28** would require the formation of a new PP bond. A sulfur atom donor is not expected to cause the reduction of a phosphorus−sulfur cage under the mild conditions of these reactions (carbon disulfide and 0−25 °C). Therefore, structures **8** and **26** are the only two that need be considered for α-P_4S_6, and the conclusion one must draw is that the reaction of α-P_4S_5 to give α-P_4S_6 is the oxidation of a trivalent phosphorus.

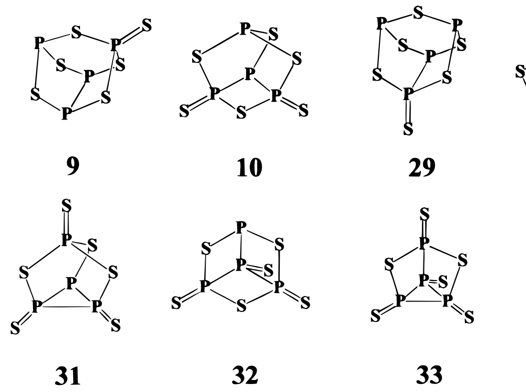

Figure 5. The seven C_s isomers of P_4S_6.

The chemistry of β-P_4S_5, as discussed below, gives further weight to the assignment of structure **8** to α-P_4S_6. In both of the first two reactions of β-P_4S_5 the faster (or only) oxidation is on the phosphorus of higher formal oxidation state. Thus, only the P^{III} phosphorus atoms are oxidized in β-P_4S_5, and the P^{III} site is more rapidly oxidized than the P^{II} sites in β-P_4S_6. This ordering would be upheld for α-P_4S_5 only if α-P_4S_6 has structure **8**. The reaction of α-P_4S_5 to give **26** requires the oxidation of a formally P^{I} center.

What about γ-P_4S_6? Studies involving both short reaction times and substoichiometric oxidations of α-P_4S_5 argue that γ-P_4S_6 is a first-formed product of the oxidation of α-P_4S_5. There are seven isomers of P_4S_6, shown in Figure 5, that have the necessary symmetry to give rise to the observed AB_2C ^{31}P NMR spectrum: P_1, 169.5 ppm; $P_{2,3}$, 103.1 ppm; P_4, 58.4 ppm; coupling constants $J_{1,2-3} = 38.7$ Hz, $J_{1,4} = 46.7$ Hz, $J_{2-3,4} = 298.8$ Hz. It is difficult to draw straightforward conversions that transform **5** into any of the products **30**−**33**. Structure **9** is already known to be β-P_4S_6. It is also well-known that the substructure P−P=S displays large coupling constants, typically larger than 200 Hz.[1,6] Of the remaining isomers, **10** and **29**, only **10** is consistent with the ^{31}P NMR spectrum. Therefore, the transformation of α-P_4S_5 into γ-P_4S_6 involves only the oxidation of a P^{II} phosphorus atom to give structure **10**.

There are three possible products from the oxidation of a trivalent phosphorus in α-P_4S_5. The third member of the group, structure **26**, is not found in this mixture of products. Unlike α-P_4S_6, extensive rearrangements would be required to transform **26** into α-P_4S_7, making it unlikely that **26** is formed competitively with **8** and **10**. If it were produced in a quantity similar to the observed isomers of P_4S_6, it would have to react rapidly either by decomposition or with another 1 mol of triphenylarsenic sulfide.

The last common product of the reaction of α-P_4S_5 with **19** is α-P_4S_7. This reaction must involve a P−P bond cleavage step. The oxidation of α-P_4S_6 (**8**) as shown in reaction c of Figure 3 is one possible mechanism for the insertion of a sulfur into the cage with formation of α-P_4S_7 (**11**). This reaction is an association−rearrangement pair that leaves the attacked phosphorus tetravalent and simply places the sulfur from **19** between a pair of phosphorus atoms. The mechanism drawn is analogous to the Baeyer−Villiger reaction of organic chemistry. If the ring expansions of the phosphorus sulfide cages involve simple rather than multistep reactions, the new sulfur must be placed adjacent to an existing tetravalent phosphorus. Thus, structure **8** should readily lead to α-P_4S_7. It is also the only structure among the group **8**, **10**, and **26** that has a bond between two trivalent phosphorus atoms, a necessary feature of **11**. Both **10** and **26** would require either reduction of a phosphorus or PP bond formation during the oxidative transformation. Assuming the above discussion is correct, then α-P_4S_6 is structure **8** and not **26**, and the major source of the α-P_4S_7 in these reactions involves the oxidation of α-P_4S_6 and not γ-P_4S_6. The oxidation of γ-P_4S_6 by the same mechanism should lead to β-P_4S_7.

The oxidation of β-P_4S_5 provides a little more insight into the dominant mechanisms and the stability of the phosphorus sulfides. The major product from the reaction of β-P_4S_5 with **19** is β-P_4S_6, structure **9**. The structures of both β-P_4S_5[10] and β-P_4S_6[7] have been determined by X-ray crystallography and are not in question. The major product of the second oxidation is, not surprisingly, α-P_4S_7, the result of the oxidation of the other P^{III} center in β-P_4S_5. β-P_4S_7 is produced by the oxidation of β-P_4S_6 at a rate between $^1/_8$ and $^1/_4$ that for the formation of α-P_4S_7 (statistically corrected), indicating the rate of oxidation in this sulfide observes the order $P^{III} > P^{II}$. The structure for β-P_4S_7 given by Blachnik is consistent with this chemistry as well as the ^{31}P NMR spectroscopy expected of structure **12**.

The dominant reaction of α-P_4S_7 with **19** under stoichiometric conditions is formation of β-P_4S_8, structure **14**. The structure assigned by Blachnik to this compound is consistent with the oxidation of one of the P^{II} phosphorus centers in α-P_4S_7. This chemistry provides strong support for both the stoichiometry and the structure of β-P_4S_8.

There are two minor components of the reaction of α-P_4S_7 with **19** that are difficult to explain. The first is a material that has been labeled γ-P_4S_8. In carbon disulfide it has the following parameters for an A_2BC coupling system: $P_{1,2}$, 95.4 ppm; P_3, 57.2 ppm; P_3, 44.2 ppm; coupling constants $J_{1-2,3} = 20.1$ Hz, $J_{1-2,4} = 30.9$ Hz, and $J_{3,4} = 156.0$ Hz. The structure of this compound was assigned to the isomer of P_4S_8 shown as compound **15**. There are only two structures with stoichiometries between P_4S_8 and P_4S_{10} that have the symmetry dictated by the NMR spectrum and no S−S bonds: structures **14** and **15**. The assignment of **14** to β-P_4S_8, derived from this and Blachnik's[7] effort, is reasonably secure, and that of **15** to γ-P_4S_8, more tenuous.

The observation of γ-P_4S_8 in this reaction mixture poses a problem: There is no straightforward way to get from α-P_4S_7 to γ-P_4S_8 without either sulfide exchange or a series of rearrangements. The fact that this material appears as a minor component of the reactions of phosphorus and sulfur detailed in the preceding article gives support to the notion that this NMR pattern corresponds to a binary phosphorus sulfide of at least moderate stability and longevity.

The second minor component has been labeled compound E and, by virtue of its coupling pattern, has four phosphorus atoms in the structure as two chemically equivalent pairs (or a multiple of this arrangement). The only structures with stoichiometries between P_4S_8 and P_4S_{10} that have the necessary symmetry have already been ascribed to α-P_4S_8 (**13**) and β-P_4S_9 (**17**). Compound E is also a transient species, being observed within the first several hours of the reaction and being absent from a spectrum taken at 24 h. Because there is no reaction between α-P_4S_7 and triphenylarsenic, the stoichiometry of compound E should be P_4S_7 or higher. Compound E, and other unassigned species in these mixtures, may be cage disulfides.

The reactions of α-P_4S_9 with **19** were observed to be either simple or complex, depending on the manner in which they were performed. If the α-P_4S_9 is completely dissolved in carbon disulfide prior to the addition of a carbon disulfide solution of **19**, the only materials observed are α-P_4S_9, P_4S_{10}, α-P_4S_7 (the sample of α-P_4S_9 contained 5−10% α-P_4S_7), and β-P_4S_8, made from the residual α-P_4S_7. The relative quantity of the sum of the α-P_4S_7 and β-P_4S_8 concentrations remained roughly constant through the course of the reaction and well afterward, indicating no reduction of α-P_4S_9 by the triphenylarsenic formed in the

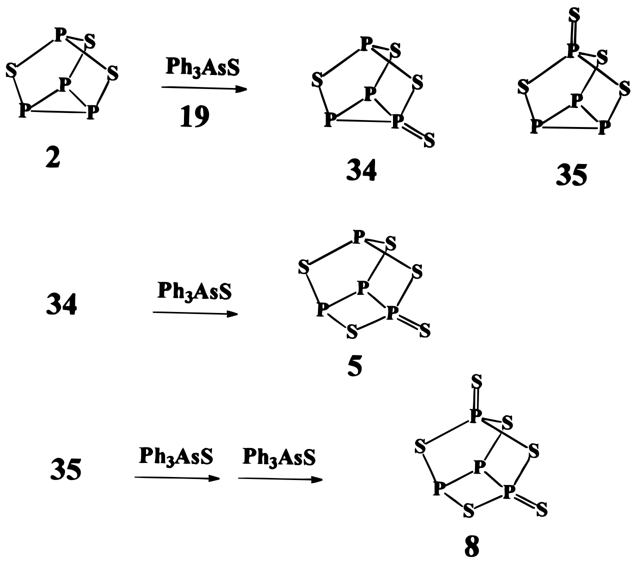

Figure 6. Possible intermediates in the reaction of P_4S_3 with **19**. See text for details.

reaction. If the α-P_4S_9 was present as a solid during the reaction, several other species were formed, not as spurious products but rather as the consistently observed outcome of reactions run with solid sulfides present. These experiments were not included in Table 1.

The reactions of P_4S_{10} with **19** were decidedly dull. The small amount of α-P_4S_9 present in the sample was converted to P_4S_{10}; no other reactions were apparent. In this system, it did not matter whether the phosphorus sulfide was completely dissolved or not. None of the unusual products mentioned above were observed, indicating that the unusual species from the oxidations of solid α-P_4S_9 are not the result of oxidation of P_4S_{10} either as a solid or in solution.

The reaction of P_4S_3 with **19** bears little resemblance to the calm and seemingly rational chemistry displayed by the higher sulfides. The first difference is the rate of reaction. P_4S_3 reacts so slowly that within the first 30 min at room temperature no reaction is visible by ^{31}P NMR spectroscopy. By contrast, all of the other sulfides show extensive or complete reaction within this same time period. Second, there are no products of intermediate sulfur content. The lowest sulfide observed is α-P_4S_7. Though there are countless paths that link P_4S_3 with α-P_4S_7, the formation of either **34** or **35**, as shown in Figure 6, is consistent with the chemistry of the higher sulfides. Only one more oxidation by **19** is required to transform **34** into α-P_4S_5. Similarly, **35** can be converted to α-P_4S_6 by two successive oxidations at the same phosphorus. The very slow reaction between P_4S_3 and **19** dictates that α-P_4S_5 and α-P_4S_6 should not be observed in these oxidations; these intermediate sulfides would be produced in the presence of a large excess of **19**, leading to continued and extensive oxidation. There are observed in these oxidations only low concentrations of α-P_4S_7, β-P_4S_8, α-P_4S_9, and P_4S_{10}, as shown in Table 1.

The reactions of two phosphorus sulfides with triphenylantimony sulfide (**21**) were also investigated, but the results were not as straightforward as those obtained with triphenylarsenic sulfide. The principle reason for the difficulty derives from the self-reaction of **21**. In all solvents studied, **21** undergoes a second-order disproportionation reaction to form triphenylantimony (**22**) and sulfur. The sulfur product of this disproportionation is expected to be an oxidizing species in its own right. Since the effective sulfur donor changes from triphenylantimony sulfide to a form of sulfur during the reaction, a great deal of mechanistic insight is lost.

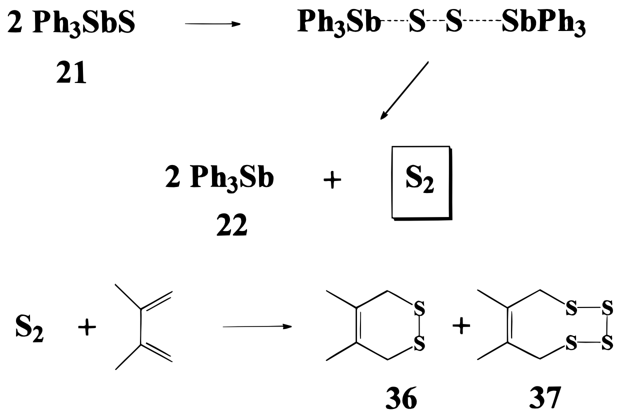

Figure 7. Disproportionation of **21** and the products of the reaction of S_2 with 2,3-dimethylbutadiene.

The simplest explanation for the second-order decay of **21** is shown in Figure 7. Two molecules of triphenylantimony sulfide are simultaneously reduced with the formation of a molecule of S_2. The reaction could occur in one step as drawn or the intermediate formation of triphenylantimony. The rate at which the disulfide decomposes to S_2 or some other species would have to be fast relative to its formation because it is not observed by NMR spectroscopy. Disulfur, S_2, is a transient species isoelectronic with singlet oxygen and has been the object of some interest for the preparation of organic disulfides.[16−19] The products of the reaction of S_2 with 2,3-dimethylbutadiene have served as markers for its formation.[16] At high concentration in a mixture of CS_2 and the butadiene, the expected disulfide and tetrasulfide products, **36** and **37**, were formed. They were identified by their ^{1}H and ^{13}C NMR spectra. There are other possible explanations for the second-order kinetics and the formation of **36** and **37**, but the formation of S_2 is consistent with both the kinetics and the formation of products believed to arise from the chemistry of S_2.

Conclusions. The triphenylarsenic and triphenylantimony sulfides have been shown to rapidly oxidize most of the known binary phosphorus sulfides. Oxidation of a cage phosphorus by the attachment of an exocyclic sulfur is the predominant mode of reactivity. The relative rates of these oxidations observe the order $P^{III} > P^{II} > P^{I}$. Oxidation of a PP bond to make a P−S−P group is slower but well within the capabilities of the reagent. Mechanisms for these oxidations are easily drawn from the atom transfer and addition−elimination mechanisms found in classical inorganic chemistry. These oxidations were used to prepare several phosphorus sulfides (α-P_4S_6 and β-P_4S_8) and to aid in the assignment of structures to two others (γ-P_4S_6 and γ-P_4S_8). The unusual disproportionation reaction of triphenylantimony sulfide was observed and a case made for the formation of disulfur, S_2.

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Supporting Information Available: Listings of ^{31}P NMR data, representative NMR spectra, and plots of kinetic data (13 pages). Ordering information is given on any current masthead page.

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