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Scheme 1.cdx Scheme 2.cdx

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Insertion of Methylthiirane into the P-I Bonds of α -P₄S₃I₂

Bruce W. Tattershall*, Nicholas S. Geneux, Kathryn E. Holmes, Michael D. Hargreaves and Glenn McMorro

Keywords: Phosphorus; Sulfur heterocycles; Insertions; Chiral Cage; NMR (³¹P, ¹³C)

Abstract. *Rac*-methylthiirane inserted into the P–I bonds of α -P₄S₃I₂, giving two diastereomers of *exo,exo*- α -P₄S₃(SCHMeCH₂I) and three diastereomers of *exo,exo*- α -P₄S₃(SCHMeCH₂I)₂, as kinetic products, identified by ³¹P and ¹³C NMR in the reaction solutions. Ab initio modelling, using the DF MPW1PW91 method, showed that corresponding products containing the SCH₂CHMe substituent should be more stable, but only α -P₄S₃(SCHMeCH₂I)(SCH₂CHMe) was suggested by the NMR evidence as a lower yield product. The initially formed thiolates were sulfurised by further methylthiirane on

heating or in the presence of the sulfur transfer catalyst Re(O)Cl₃(PPh₃)₂, to give low concentrations of α -P₄S₃(S)(SCHMeCH₂I) and α -P₄S₃(S)(SCHMeCH₂I)₂, in which a 1-coordinate sulfur atom was attached to a phosphorus atom carrying the thiolate group. The number of diastereomers appropriate for only one orientation of the terminal sulfur relative to the cage skeleton was found in significant concentration in each case, in contrast to previous work on sulfurisation of α -P₄S₃ diamides.

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Introduction

A large number of phosphorus sulfide cage compounds α -P₄S₃XY **1**, where X and Y are non-metal centred groups, have been made by substitution reactions starting from the readily prepared α -P₄S₃I₂. Recently, these have included compounds containing chiral amido substituents [1,2]. The α -P₄S₃ skeleton involves only three-coordinate phosphorus atoms, formally carrying lone pairs of electrons. While many binary phosphorus sulfides contain four-coordinate phosphorus, where the lone pair has been replaced by one-coordinate sulfur, hardly any P–S cage compounds are known which have other exocyclic substituents, as well as one-coordinate sulfur on phosphorus. We reported previously that α -P₄S₃ diamides, e.g. α -P₄S₃(NPrⁱ)₂, reacted with S₈ under photolysis by visible light, to give three isomers of α -P₄S₃(S)(NPrⁱ)₂ **2**, in which one of the phosphorus atoms carried a terminal sulfur atom [3]. A similar reaction of α -P₄S₃I₂ itself gave no corresponding new phosphorus sulfide iodides, which could have been valuable intermediates in making new families of derivatives.

Since then, we have examined methylthiirane **3**, as a reagent for sulfurisation of phosphorus, in the presence of Re(O)Cl₃(PPh₃)₂ as an homogenous sulfur transfer catalyst [4]. This reacted readily at room temperature in solution

with α -P₄S₃(NPrⁱ)₂ to give good ³¹P NMR spectra of some of the isomers of α -P₄S₃(S)(NPrⁱ)₂ reported previously, along with related ³¹P NMR spectra of new phosphorus sulfide amide cage compounds, which have not been identified [5]. In the present work we have investigated whether the methylthiirane method could be used also to sulfurise α -P₄S₃I₂.

((Insert Scheme 1 here, single column width))

Instead of sulfurisation, with elimination of propene, methylthiirane inserted into one or both P–I bonds of α -P₄S₃I₂, to give the new thiolato derivatives α -P₄S₃(SCHMeCH₂I) and α -P₄S₃(SCHMeCH₂I)₂, identified in the reaction mixture by ³¹P and ¹³C NMR. Starting from racemic methylthiirane, the expected two diastereomers of the thiolate iodide, and three diastereomers of the dithiolate, were observed. In the presence of the rhenium catalyst, or on heating the mixture to 60 °C without the catalyst, these reacted further to give low concentrations of α -P₄S₃(S)(SCHMeCH₂I) (two diastereomers) or α -P₄S₃(S)(SCHMeCH₂I)₂ (four diastereomers). Methylthiirane is known to insert into a P–Cl bond of MePCL₂ at 60 °C [6]. Simple α -P₄S₃ dithiolates **1** (X = Y = SMe, SEt or SPh) are known [7], but in the α -P₄S₃ thiolate iodide series, only α -P₄S₃(SPh)I has been reported, as being formed in less than the expected relative quantities in the reaction of α -P₄S₃I₂ with PhSH and Et₃N [8]. Its ³¹P NMR spectrum had been published already [9].

Results and Discussion

Reaction of α -P₄S₃I₂ with methylthiirane, and observed products

The reactions gave homogenous solutions in which relative quantities of phosphorus-containing products were estimated

by ^{31}P NMR integration. Because the spectra contained three regions of strongly overlapping multiplets (see below), this method was less accurate than usual, but the qualitative conclusions given here are believed to be correct.

Ratio $\alpha\text{-P}_4\text{S}_3\text{I}_2 : \text{CH}_3(\text{CHCH}_2\text{S}) = 1 : 2$. *Rac*-methylthiirane was mixed with a ca. 0.05 mol dm^{-3} solution of $\alpha\text{-P}_4\text{S}_3\text{I}_2$ in CS_2 . After 22 hours at 21°C , the visibly unchanged solution contained mostly unreacted $\alpha\text{-P}_4\text{S}_3\text{I}_2$, along with $\alpha\text{-P}_4\text{S}_3(\text{SCHMeCH}_2\text{I})\text{I}$ and a little $\alpha\text{-P}_4\text{S}_3(\text{SCHMeCH}_2\text{I})_2$. Half the solution was then heated under reflux at 60°C for 5 hours. The dithiolate $\alpha\text{-P}_4\text{S}_3(\text{SCHMeCH}_2\text{I})_2$ was now the major constituent (49 mol%). Some $\alpha\text{-P}_4\text{S}_3\text{I}_2$ (14 mol%) and $\alpha\text{-P}_4\text{S}_3(\text{SCHMeCH}_2\text{I})\text{I}$ (18 mol%) remained, and traces of the decomposition products $\alpha\text{-P}_4\text{S}_4$, $\alpha\text{-P}_4\text{S}_5$ and P_4S_7 had appeared. With hindsight, $\alpha\text{-P}_4\text{S}_3(\text{S})(\text{SCHMeCH}_2\text{I})\text{I}$ was just detectable. The peaks representing the remaining 19 mol% of the major components were assigned hypothetically to the unsymmetric di-insertion product $\alpha\text{-P}_4\text{S}_3(\text{SCHMeCH}_2\text{I})(\text{SCH}_2\text{CHIME})$.

Of the methylthiirane taken, 23% was unaccounted for by the phosphorus-containing products. The statistical distribution $\alpha\text{-P}_4\text{S}_3\text{I}_2 : \alpha\text{-P}_4\text{S}_3(\text{SCHMeCH}_2\text{I})\text{I} : \alpha\text{-P}_4\text{S}_3(\text{SCHMeCH}_2\text{I})_2$ for a substituent redistribution reaction is 8 : 41 : 51, based on the quantities of iodide and $\text{SCHMeCH}_2\text{I}$ ligands found in these compounds. This may be compared with the observed distribution 17 : 23 : 60, showing that a redistribution equilibrium probably was not reached. While the related cage compound $\text{P}_3\text{Se}_4\text{I}$ undergoes a rapid skeletal rearrangement reaction in solution in CS_2 , involving simultaneous exchange of the exocyclic iodide substituent between phosphorus atoms, no dynamic NMR effects were observed for the corresponding thiolate $\text{P}_3\text{Se}_4(\text{SEt})$, even at 370 K [10].

The other half of the original solution was instead treated with ca. 0.05 mole equivalent of $\text{Re}(\text{O})\text{Cl}_3(\text{PPh}_3)_2$ (compared with the original methylthiirane content of this portion), giving a dark brown solution, which was stirred at room temperature for 5 hours. The distribution of phosphorus cage compounds was mostly unchanged by this, except that traces of the two diastereomers of $\alpha\text{-P}_4\text{S}_3(\text{S})(\text{SCHMeCH}_2\text{I})\text{I}$ now were clearly visible, so that their spectra could be fitted (see below).

Ratio $\alpha\text{-P}_4\text{S}_3\text{I}_2 : \text{CH}_3(\text{CHCH}_2\text{S}) = 1 : 1$. In this experiment, double the concentration of $\alpha\text{-P}_4\text{S}_3\text{I}_2$ was used, to favour the formation of $\alpha\text{-P}_4\text{S}_3(\text{SCHMeCH}_2\text{I})\text{I}$, and, immediately after mixing, the solution was heated to 60°C for 23 hours. Under these conditions, 55% of the methylthiirane taken was unaccounted for by the phosphorus-containing products. The resulting solution contained $\alpha\text{-P}_4\text{S}_3\text{I}_2$, $\alpha\text{-P}_4\text{S}_3(\text{SCHMeCH}_2\text{I})\text{I}$ and $\alpha\text{-P}_4\text{S}_3(\text{SCHMeCH}_2\text{I})_2$ in the ratio 61 : 33 : 6. This was similar to the statistical distribution 60 : 35 : 5, so a redistribution equilibrium may have been attained after the longer heating period. The lower concentration of $\alpha\text{-P}_4\text{S}_3(\text{SCHMeCH}_2\text{I})_2$ relative to $\alpha\text{-P}_4\text{S}_3(\text{SCHMeCH}_2\text{I})\text{I}$ allowed more of the spectra of the two diastereomers of the thiolate iodide to be revealed, and good computer fits to be obtained.

Ratio $\alpha\text{-P}_4\text{S}_3\text{I}_2 : \text{CH}_3(\text{CHCH}_2\text{S}) = 1 : 4$. Here, twice as much methylthiirane was taken, compared with the first

experiment, and the solution was heated to 60°C for 23 hours, with the intention not only of favouring the formation of $\alpha\text{-P}_4\text{S}_3(\text{SCHMeCH}_2\text{I})_2$ and the supposed $\alpha\text{-P}_4\text{S}_3(\text{SCHMeCH}_2\text{I})(\text{SCH}_2\text{CHIME})$, but of removing $\alpha\text{-P}_4\text{S}_3\text{I}_2$ and the $\alpha\text{-P}_4\text{S}_3$ thiolate iodide, in order to give clearer spectra of these dithiolates. Because compounds containing P–I bonds were used up, the resulting solution was pale lemon instead of bright yellow. The ^{31}P NMR spectrum showed no $\alpha\text{-P}_4\text{S}_3\text{I}_2$ nor $\alpha\text{-P}_4\text{S}_3(\text{SCHMeCH}_2\text{I})\text{I}$ remaining. The two dithiolates $\alpha\text{-P}_4\text{S}_3(\text{SCHMeCH}_2\text{I})_2$ and $\alpha\text{-P}_4\text{S}_3(\text{SCHMeCH}_2\text{I})(\text{SCH}_2\text{CHIME})$ were found in the ratio 69 : 31, which was similar to the ratio 72 : 28 estimated in the first experiment. The spectra of all three diastereomers of $\alpha\text{-P}_4\text{S}_3(\text{SCHMeCH}_2\text{I})_2$ could now be fitted, but the four diastereomers of $\alpha\text{-P}_4\text{S}_3(\text{SCHMeCH}_2\text{I})(\text{SCH}_2\text{CHIME})$ were seen only as a region of overlapping multiplets corresponding to one of the phosphorus positions. The regions representing the other three of the four phosphorus atoms per diastereomer were too obstructed, by the spectra of the major product, for analysis, so coupling constants could not be obtained and assignment of the minor product to $\alpha\text{-P}_4\text{S}_3(\text{SCHMeCH}_2\text{I})(\text{SCH}_2\text{CHIME})$ remains an hypothesis.

The four diastereomers of the monosulfurised dithiolate $\alpha\text{-P}_4\text{S}_3(\text{S})(\text{SCHMeCH}_2\text{I})_2$ were observed to constitute about 7 mol% of the measured product. Sets of overlapping multiplets were found for three of the phosphorus atoms, with only one set of multiplets being obscured. While, consequently, these spectra also could not be fitted, the spin systems were almost first order, so approximations could be made to all of the phosphorus NMR parameters, except for one set of chemical shifts, making the identification fairly certain. Addition of a further two molar equivalents of methylthiirane, in case the original excess had now polymerised, and 0.1 molar equivalents of the rhenium catalyst, was found after 8 hours at room temperature to have given further amounts of the same set of isomers of $\alpha\text{-P}_4\text{S}_3(\text{S})(\text{SCHMeCH}_2\text{I})_2$, but also many new overlapping multiplets in the same regions, making analysis of the spectrum too difficult.

Direction of insertion; isomers and diastereomers of products

Iodine is somewhat more electronegative than phosphorus, on any of the common scales, and attack by a P–I bond on methylthiirane may be thought of as starting with nucleophilic attack, by the partially charged iodine atom, on a ring carbon atom. The LUMO of $\text{CH}_3(\text{CHCH}_2\text{S})$, calculated at the RHF/3-21G* level, is σ antibonding with respect to both C–S bonds. The attacking iodine will experience positive electrostatic potential (ESP) at either ring carbon atom, but the CH_2 group carries the most accessible lobe of the LUMO. An image of methylthiirane as a space-filling model, with a surface of the LUMO (contour level 0.015) protruding from it, and ESP mapped upon the LUMO (blue and violet positive, green negative), is given in the Electronic Supporting Information (ESI). It may be predicted that iodine will attack the CH_2 group, causing heterolytic cleavage of the $\text{CH}_2\text{--S}$ bond, and formation of the $\dots\text{I--CH}_2\text{CH}(\text{Me})\text{S}^{\delta-}$ pendant group (Scheme 2). Attack by the partially charged sulfur atom on phosphorus will finally cause cleavage of the P–I bond, giving a $\text{SCHMeCH}_2\text{I}$ substituent in the major kinetic product. Alternative attack of iodine on the less accessible

lobe of the LUMO, at the CHMe group, would lead to a SCH₂CHIME substituent in a minor kinetic product.

((Insert Scheme 2 here, double column width))

The further possibility, of initial attack by thiirane sulfur on phosphorus, followed by orientation of the still intact three-membered ring to allow intramolecular attack by the iodine on the CH₂ group, seems much less likely because (a) solvent CS₂ would compete more effectively with neutral than with negatively charged sulfur for coordination to phosphorus; (b) the concerted mechanism would involve a 4-membered instead of a 5-membered ring; and (c) orientation of the coordinated thiirane, to present a σ* orbital at CH₂ to the iodine, would be more difficult.

Modelling the products by ab initio methods, at a sufficient level to predict rigorously the more thermodynamically stable, would be a major undertaking because of the number of bond rotamers which should be considered. This is a severe problem for any α-P₄S₃ derivatives which carry exocyclic substituents with several possibilities for internal rotations, as shown recently for amide substituents [11]. Software, which uses force field methods to search automatically for conformers, cannot take account of nonbonded interactions between the substituent conformers and the phosphorus sulfide cage, so searching must be done at an ab initio level and, in our case, set up by hand. Models of one rotamer for each of the two diastereomers of α-P₄S₃(SCHMeCH₂I), three diastereomers of α-P₄S₃(SCHMeCH₂I)₂, four diastereomers of α-P₄S₃(SCHMeCH₂I)(SCH₂CHIME), and for the three diastereomers of α-P₄S₃(SCH₂CHIME)₂ were obtained at the RHF/3-21G* level and the geometries refined using the density functional MPW1PW91 method. The basis set used with this consisted of Ahlrichs svp basis on all atoms except iodine, for which 3-21G* was taken. Rotatable molecular structure diagrams are presented for these models, along with their energies, in the ESI. During the search for conformers, other rotamers of some of the molecules were examined, but the results are not presented because the predicted energies were significantly higher and the set given is believed to be sufficient to give a useful predictive ability.

The α-P₄S₃ cage is chiral, with α-P₄S₃I₂ existing (and crystallising) as a racemic mixture of enantiomers **1a** and **1b**. These were represented as (SS) and (RR) respectively in our work on chiral amide derivatives [1,2], showing the configurations of the phosphorus atoms P_B and P_D to which the iodide substituents were attached. Chiralities of substituents were written outside of the parentheses, to the left for substituent X and to the right for Y (Scheme 1). The chirality symbol for phosphorus remained the same when amide replaced iodide. This is not so for replacement of iodide by thiolate, when the (SS) diiodide would give e.g. a thiolate iodide **R(RS)** and then a dithiolate **R(RR)R** or **R(RR)S**, even though the visual shapes at phosphorus do not change. We will therefore use here only (**1a**) and (**1b**) to refer to these visual shapes in Scheme 1. Reaction with racemic methylthiirane would give, as the first product, two diastereomers **R(1a)** and **S(1a)** of α-P₄S₃(SCHMeCH₂I) or of α-P₄S₃(SCH₂CHIME)I, along with their enantiomers, indistinguishable from them by NMR, **S(1b)** and **R(1b)** respectively. Each isomer would thus show two overlapping NMR spectra.

Some diastereomeric excess could be formed in the product, caused by a preference for matching (or mismatching) chirality in the rate-determining step of the reaction. As both reagents were racemic, and a pair of enantiomers, e.g. **R(1a)** and **S(1b)** could account for complete use of both reagents, formation of diastereomeric excess does not depend on partial reaction of one racemic compound, as it would for kinetic resolution using an enantiomerically pure resolving agent.

The dithiolates α-P₄S₃(SCHMeCH₂I)₂ or α-P₄S₃(SCH₂CHIME)₂ would be formed as mixtures of the three diastereomers **R(1a)R**, **S(1a)S** and **R(1a)S**. If chiral preference on one side of the cage is independent of the chirality of the distant substituent, the unsymmetric diastereomer **R(1a)S** should constitute the statistical 50% of the mixture of diastereomers, with the symmetric diastereomers **R(1a)R** and **S(1a)S** constituting either more or less than 25% of the mixture each [2].

If atom labelling in the mixed dithiolate α-P₄S₃(SCHMeCH₂I)(SCH₂CHIME) is as written (Scheme 1, **1**, X = SCHMeCH₂I, Y = SCH₂CHIME), either substituent may have matching or mismatching chirality, so there would be four diastereomers **R(1a)R**, **S(1a)R**, **R(1a)S** and **S(1a)S** (each as a pair with the corresponding enantiomer).

Taking statistical weightings into account, the ab initio models predict that if equilibrium were reached between all structural isomers of α-P₄S₃(SCHMeCH₂I)₂, and between all the diastereomers of each of them, the ratio α-P₄S₃(SCHMeCH₂I)₂ : α-P₄S₃(SCHMeCH₂I)(SCH₂CHIME) : α-P₄S₃(SCH₂CHIME)₂ would be 11 : 37 : 52. The major thermodynamic product would be the minor kinetic product. For the structural isomer α-P₄S₃(SCH₂CHIME)₂, the predicted diastereomer ratio was **R(1a)R** : **R(1a)S** : **S(1a)S** = 36 : 47 : 16, whereas for α-P₄S₃(SCHMeCH₂I)₂ it was 30 : 48 : 22. Phosphorus NMR spectra for two symmetric diastereomers were observed, and although overlapping peaks precluded their relative integration, the observed relative intensity was much more similar than the 2.22 : 1 predicted for the SCH₂CHIME product, and supports their attribution to the kinetic product α-P₄S₃(SCHMeCH₂I)₂. The observed relative amount of the mixed dithiolate α-P₄S₃(SCHMeCH₂I)(SCH₂CHIME) was then much less than predicted. We conclude that isomerisation of the SCHMeCH₂I substituent to SCH₂CHIME did not reach equilibrium, and that α-P₄S₃(SCH₂CHIME)₂ was not observed. The best evidence, that the major product was α-P₄S₃(SCHMeCH₂I)₂, came from the ¹³C NMR spectrum and from ¹³C, ¹H correlation experiments on the product of the 1 : 4 reaction, described below.

All of these α-P₄S₃ compounds have been assumed to carry exo,exo-substituents, since the NMR parameters, of those whose spectra have been analysed, correspond to the pattern found for previously known exo,exo-α-P₄S₃ compounds, rather than the less common and normally less stable exo,endo-α-P₄S₃ configuration. Inversion at phosphorus on the NMR timescale is not expected. Sulfurisation at P_B, however, could go either with retention or inversion of configuration, as found for sulfurisation of α-P₄S₃ amides [3]. Each such isomer would consist of two diastereomers, **R(2a)** and **S(2a)**, for α-P₄S₃(S)(SCHMeCH₂I)I, as in the unsulfurised compound,

but for α -P₄S₃(S)(SCHMeCH₂I)₂ there would now be four, since the P_B and P_D sides of the molecule are differentiated, as for α -P₄S₃(SCHMeCH₂I)(SCH₂CHIME) above.

Assignment of NMR spectra

¹³C NMR spectra of the product from the 1 : 4 reaction.

Besides singlets due to unreacted methylthiirane (δ = 29.94 (CH), 26.77 (CH₂) and 21.85 (CH₃) [12], the ¹³C{¹H} spectrum showed major multiplets at δ = 45.37, 22.74 and 13.41, shown by comparison with the proton-coupled spectrum and a DEPT experiment to be due to CH (¹J_{CH} = 146 Hz), CH₃ (128 Hz) and CH₂ (152 Hz) respectively. Each of these appeared as four peaks, corresponding to one diastereomeric splitting and one related to ¹³C-³¹P coupling, except for the multiplet due to CH, which showed an extra small doublet splitting of ca. 3 Hz, associated with longer range ¹³C-³¹P couplings. The main splittings were assigned to diastereomeric shift difference, rather than to the coupling to phosphorus, if they were between doublets which were more different in intensity, resulting in the following parameters for α -P₄S₃(SCHMeCH₂I)₂. Diastereomeric shift ($\delta\delta$) is given as δ (major diastereomer) - δ (minor diastereomer). CH doublet 18.6 (major), 19.7 (minor) Hz $\delta\delta$ -24.3 Hz, -0.19 ppm; CH₃ doublet 4.7 (major), 5.2 (minor) Hz, $\delta\delta$ 25.1 Hz, 0.20 ppm; CH₂ doublet 6.7 (major), 5.7 (minor) Hz, $\delta\delta$ 29.5 Hz, 0.23 ppm. The doublets for the CH₃ group were practically equal in height, so the minor/major assignment was less certain than for the other groups.

These results may be explained if carbon-phosphorus couplings and carbon diastereomeric shifts depended only on the chirality match or mismatch between the substituent and the cage phosphorus atom to which it was attached, rather than on any interaction between the two substituents. Thus, e.g., diastereomer **R(1a)S** of α -P₄S₃(SCHMeCH₂I)₂ would show a separate ¹³C NMR spectrum for each of its substituents, but one of these would be superimposed on that for diastereomer **R(1a)R**, and the other on that for diastereomer **S(1a)S**.

The order of chemical shifts between the multiplets was as might be expected for the connectivity P-S-CH(CH₃)CH₂I. CH next to sulfur is moved to high frequency: e.g. CH in (Et(Me)CHS)₂ has δ 48.28, while CH bonded to iodine would have been moved to low frequency, as in Et(Me)CHI (δ 28.5) [12].

There was one other, smaller multiplet in the ¹³C{¹H} spectrum, which could be assigned to CH₂ of the SCH₂CHIME group in the minor product α -P₄S₃(SCHMeCH₂I)(SCH₂CHIME). This was at δ 46.75. CH₂S in (PrⁿS)₂ has δ 41.21 [12]. The DEPT and proton-coupled experiments confirmed that this was a CH₂ group, though the intensity was too low for ¹J_{CH} to be measured. The ¹³C{¹H} multiplet showed major and minor doublets more different from each other in intensity than for the SCHMeCH₂I multiplets, as predicted by the ab initio energy calculations (see above). The doublet splitting was ca. 22.2 Hz for each diastereomer; $\delta\delta$ was 6.2 Hz, 0.05 ppm. The remaining, CH and CH₃, multiplets for this substituent were not found.

³¹P{¹H} spectra.

An initial exploration was made using a homonuclear ³¹P COSY measurement, on the product of the 1 : 2 reaction after heating (see above). Dense regions of peaks were centred at ca. (i) 126; (ii) 121; (iii) 116 and (iv) 104 ppm. There were strong correlation peaks for α -P₄S₃I₂ within region (i) and for α -P₄S₃(SCHMeCH₂I)₂ between regions (iii) and (iv). One set of correlation peaks in region (i) could be distinguished by position from those of α -P₄S₃I₂, and showed α -P₄S₃(SCHMeCH₂I)I in regions (i), (ii) and (iii), but not in (iv). There were correlation peaks to the same part of region (iii), from regions (i) and (ii), but no correlation peak could be found between regions (i) (P_D) and (ii) (P_B). This was because the corresponding coupling for α -P₄S₃(SCHMeCH₂I)I, ³J(P_BP_D), was very small (-1 Hz, Table 1). A third set of correlation peaks in region (i) linked it to region (iv), and were attributed to α -P₄S₃(SCHMeCH₂I)(SCH₂CHIME), for which the P_D multiplets were found in region (i) of the product of the 1 : 4 reaction, and the P_A, P_C multiplets were believed as a result of the present COSY experiment to be in region (iv). There were small correlation peaks for this compound between regions (i) and (iii), where P_B probably was located. ³J(P_BP_D) is expected to be small (c.f. -8.2 Hz in diastereomer **R(1a)S** of α -P₄S₃(SCHMeCH₂I)₂), but not as small as in α -P₄S₃(SCHMeCH₂I)I.

Hand analysis of ³¹P{¹H} spectra was followed by iterative fitting using NUMARIT [13], wherever sufficient peaks could be assigned. In those cases, chemical shifts and coupling constants are given in Table 1.

Table 1 NMR parameters for *exo,exo*- α -P₄S₃XY **1** and α -P₄S₃(S)XY **2** in solution in CS₂

	1	1	1	1	1	2	2
X ^{a)}	SR	SR	SR	SR	SR	SR	SR
Y ^{a)}	I	I	SR	SR	SR	I	I
Diastereomer	A	B	A	B	C	X	Y
(a) Coupling constants (Hz) ^{b)}							
¹ J(P _A P _B)	-289.0(2)	-290.44(9)	-288.1(5)	-289.8(5)	-287.39(3)	-377.73(2)	-378.43(3)
¹ J(P _C P _D)	-242.2(1)	-241.99(8)	-288.1(5)	-289.8(5)	-289.09(5)	-228.76(2)	-229.99(4)
² J(P _A P _C)	67.1(1)	66.9(1)	59.2(7)	58.0(8)	60.39(4)	71.86(1)	71.47(2)
² J(P _A P _D)	17.7(2)	18.1(1)	23.0(4)	22.6(5)	22.09(3)	33.98(1)	34.39(3)
² J(P _B P _C)	24.9(1)	24.74(8)	23.0(4)	22.6(5)	22.25(3)	9.02(2)	8.75(4)
³ J(P _B P _D)	-1.1(1)	-1.0(1)	-8.5(12)	-8.5(15)	-8.20(3)	9.19(3)	9.47(5)

(b) Chemical shifts (ppm)^{c)}

$\delta(P_A)$	117.32	116.73	103.94	103.88	104.53	69.36	68.21
$\delta(P_B)$	121.20	120.95	116.95	116.91	117.13	162.71	162.79
$\delta(P_C)$	114.45	114.89	103.94	103.88	103.31	139.52	143.39
$\delta(P_D)$	127.68	127.90	116.95	116.91	116.80	112.93	112.39

^{a)} SR = SCHMeCH₂I ^{b)} Standard deviations (σ) in parentheses. ^{c)} ³¹P Shifts relative to 85% H₃PO₄ - H₂O³¹P{¹H} NMR spectra of α -P₄S₃(SCHMeCH₂I)I (**1**, X = Y = (SCHMeCH₂I), Y = I).³¹P{¹H} NMR spectra of α -P₄S₃(SCHMeCH₂I)₂ (**1**, X = Y = (SCHMeCH₂I)).

The smallest chemical shift difference was $\delta(P_A) - \delta(P_C)$ (Scheme 1), which was 2.87 ppm for diastereomer A and 1.84 ppm for diastereomer B. The coupling $^2J(P_AP_C)$ was 67.1 and 66.9 Hz respectively, giving $J/\delta = 0.115$ at 202.5 MHz for diastereomer A. This was sufficiently small that all four phosphorus atoms gave strongly tented but simple multiplets which could be analysed using the first order approximation, to provide a starting point for a Numarit fit. Diastereomer B had $J/\delta = 0.179$, giving multiplets which could not be analysed in this way, but, by assuming the same couplings as in diastereomer A and estimating the differences in chemical shifts from it, a recognisable simulation was obtained. The chemical shifts and coupling constants (Table 1) were very similar to those for α -P₄S₃(SPh)I [9]. The P_D multiplet could be assigned relative to P_B, because $^1J(P_CP_D)$ had a value less negative than $^1J(P_AP_B)$, typical for α -P₄S₃ compounds with iodine attached to P_D.

The peaks assigned to P_B were sufficiently free of overlaps for integration, giving the diastereomer ratio A : B = 1.19 : 1. The ratio **R(1a)** : **S(1a)** was predicted at the ab initio MPW1PW91/svp level to be 1.09 : 1 (see ESI), suggesting that diastereomer A was **R(1a)**. The largest diastereomeric difference in P-P coupling constants, for $^1J(P_AP_B)$, was small (1.4 Hz), but its sign was in agreement with the ab initio prediction that diastereomer **R(1a)** had the longer P_A-P_B bond (by 0.0017 Å), and so might be expected to have the less negative 1J coupling constant, as observed for diastereomer A. The longer predicted bond may be associated with a torsion angle C-S-P_B-P_A nearer to 90°, allowing more π interaction between a thiolate sulfur 'lone pair' and the σ^* P_B-P_A orbital. Previously we have demonstrated a similar connection between observed $^1J(P_AP_B)$ and calculated torsion angle to the mean bonding plane of nitrogen in bond rotamers of an amide [2, 14], where the differences, both in coupling constant and in torsion angle, were much larger than in the present case.

At 202.5 MHz, a number of sharp peaks for the unsymmetric diastereomer **R(1a)S** could be distinguished from the typical AA'MM' spectra of the symmetric diastereomers **R(1a)R** and **S(1a)S**, which had rather broader peaks containing more overlapping transitions. Since assignments to absolute configuration are only hypotheses in this work, the symmetric diastereomers are referred to experimentally as A and B, in order of relative abundance, and the unsymmetric diastereomer as C, as in previous work [2].

Diastereomer C. This had an internal diastereomeric shift $\delta(P_A) - \delta(P_C)$ of 1.22 ppm, and a coupling constant $^2J(P_AP_C)$ of 60.4 Hz, giving J/δ 0.244 at 202.5 MHz. In contrast, although $\delta(P_B) - \delta(P_D)$ was only 0.33 ppm, $^3J(P_BP_D)$ was -8.20, so the corresponding $|J/\delta|$ was only 0.122. The spin system could be analysed as AFMN and the MN region (P_A and P_C, region (iv), above) treated by subspectral analysis. This region was recognised because the outermost four peaks on each side showed the typical separations of half of a bridgehead phosphorus multiplet in a α -P₄S₃ compound. The hand analysis yielded all of the coupling constants except for $^3J(P_BP_D)$, along with $\delta(P_A)$ and $\delta(P_C)$. An initial value of -8 Hz was taken for $^3J(P_BP_D)$, by analogy with α -P₄S₃(SEt)₂, and the diastereomeric shift $\delta(P_B) - \delta(P_D)$ was found by trial and error simulations until one could be recognised and the spectrum fitted. The resulting shifts were translated to an operating frequency of 121.5 Hz, allowing a spectrum at this lower field strength also to be recognised and fitted, confirming the assignment of peaks in both cases.

Diastereomers A and B. For each diastereomer, each multiplet ((P_BP_D), region (iii), and (P_AP_C), region (iv)) is expected to consist of two strong peaks and two AB subspectra. At 202.5 MHz in region (iv), the two strong peaks separated by $N (= ^1J(P_AP_B) + ^2J(P_BP_C))$ were resolved for each diastereomer. Diastereomer A, at higher shift $\delta(P_A)$, had measurably smaller $|N|$ (by 2.1 Hz), allowing the higher frequency spectrum in region (iii) also to be assigned to diastereomer A, even though the relative abundance could not be seen there, because of overlapping peaks. Coupling constants found for α -P₄S₃(SCHMeCH₂I)I and for α -P₄S₃I₂ were then used to predict couplings for α -P₄S₃(SCHMeCH₂I)₂, by means of our 'balancing rules' [2]. Numarit simulations from these allowed enough peaks of each diastereomer to be identified, for the spectra to be fitted. The diastereomeric shifts $\delta(P_B) - \delta(P_D)$ and particularly $\delta(P_A) - \delta(P_C)$ were larger within diastereomer C than between diastereomers A and B.

Higher abundance, higher chemical shifts, less negative $^1J(P_AP_B)$ and more positive $^2J(P_BP_C)$ (giving smaller $|N|$) suggested that diastereomer A had the same chirality match,

between cage and substituent, as diastereomer A of α -P₄S₃(SCHMeCH₂I)I. The ab initio calculations predicted that the more stable diastereomer **R(1a)R** would have, as for α -P₄S₃(SCHMeCH₂I)I, a longer bond P_A–P_B and a smaller torsion angle C–S–P_B–P_A. Probably diastereomer A was **R(1a)R** and diastereomer B was **S(1a)S**. In diastereomer C, the side of the molecule with the less negative ¹J(P_AP_B) and the higher chemical shifts δ (P_A) and δ (P_B), probably carried the R chirality substituent, so writing the chirality as **R(1a)S** rather than as **S(1a)R**, would be correct in terms of the atom labelling in Scheme 1 and the NMR parameter labelling in Table 1. The ab initio calculations predicted that P_A–P_B in **R(1a)S** is longer than P_C–P_D, by 0.0019 Å.

³¹P{¹H} NMR spectra of α -P₄S₃(SCHMeCH₂I)-(SCH₂CHMe)

The group of peaks in region (i) of the spectrum of the 1 : 4 product, attributed to P_D as a result of the COSY experiment (above), were not individually assigned because of lack of enough information on chemical shifts to provide a recognisable simulation for any of the diastereomers. The appearance of the simulated P_D multiplet depended particularly strongly on the internal chemical shift δ (P_A)– δ (P_C). The statistically weighted predicted relative abundances of the diastereomers was 43 : 19 : 13 : 25, in the order given in the ESI. It would have been possible for the observed group of peaks to have consisted of one major spectrum and other, progressively more minor spectra, but probably not to have been made up of several components of similar intensity. The chemical shift δ (P_D) was ca. 126.1 ppm.

³¹P{¹H} NMR spectra of α -P₄S₃(S)(SCHMeCH₂I)I (2, X = (SCHMeCH₂I), Y = I)

These nearly first order spectra were recognised from the high chemical shifts of the P_B multiplets (162.8 ppm, Table 1) and low chemical shifts of P_A (68.8 ppm), which made them appear in relatively clear regions of the spectral range. The high and low shifts are characteristic of addition of a terminal sulfur atom at P_B, as is the large coupling they share [3]. The P_C and P_D multiplets could then be identified as sharing other couplings with P_A or P_B. The spectra could be distinguished from those of other sulfuration products because their intensities varied together over several product mixtures, and clearly represented two diastereomers, as required for one the stereoisomers of α -P₄S₃(S)(SCHMeCH₂I)I, rather than the four diastereomers of α -P₄S₃(S)(SCHMeCH₂I)₂, which also were present in some of the mixtures (see below).

The two diastereomers were of similar abundance. To avoid implying a correspondence with the configurations of diastereomers A and B of α -P₄S₃(SCHMeCH₂I)I, we refer to the present pair as X and Y. For P_B, the diastereomeric shift $\delta\delta$ was -0.08 ppm, or -10 Hz at 121.5 MHz. Both ²J(P_BP_C) and ²J(P_BP_D) had values of ca. 9 Hz, so the P_B multiplets together appeared at this operating frequency as a doublet (¹J(P_AP_B)) of quartets. The diastereomeric shifts for P_D and P_A were larger, so that the diastereomer multiplets were interleaved, while $\delta\delta$ was exceptionally large for P_C (-3.87 ppm), giving separate multiplets. In a α -P₄S₃ amide iodide (**1**, X = NHCH(Me)Ph, Y = I), it was P_D, carrying the iodide substituent, which showed the greatest diastereomeric

shift (2.98 ppm) [1]. Diastereomeric differences in coupling constants were small, making it difficult to determine which of the two multiplets in each region belonged to a particular diastereomer. Evidence for this association was sought by trial and error fits, interchanging the assignment in each region in turn. The best fits are presented in Table 1, but the results are not certain: i.e. the sign of at least one of the diastereomeric shifts might be the opposite.

The distribution of chemical shifts and coupling constants parallels that for either invertomer of α -P₄S₃(S)(NPrⁱ)₂ (**2**, X = Y = NPrⁱ) [3], either with the 1-coordinate sulfur endo to the cage or exo to it. The compounds are sufficiently dissimilar that an assignment to one rather than the other stereochemistry cannot be made by this analogy. Sulfuration of the diamino compound gave the stereoisomers in about 3 : 1 ratio, whereas in the present experiments only one such isomer was identified. Comparing α -P₄S₃(S)(SCHMeCH₂I)I with α -P₄S₃(SCHMeCH₂I)I, each of the four chemical shifts changed on sulfuration in the same direction and with a similar magnitude of change to those in the α -P₄S₃(S)(NPrⁱ)₂ case. The three coupling constants to P_A changed in the same directions, but ¹J(P_AP_B) became more negative by a larger amount (88.7 Hz) than did the corresponding coupling in α -P₄S₃(S)(NPrⁱ)₂ (21.9 Hz). For the analogous α -P₄S₃(S)(NMePh)₂, the change was 41.6 Hz [3]. Probably the greater π to σ^* donor ability of the amide substituents, particularly NPrⁱ, caused a weakening of the P_A–P_B bond to compensate for the other effects of increasing oxidation state of P_B on sulfuration. In α -P₄S₅, where there are no exocyclic substituents except for one 1-coordinate sulfur atom, the difference in ¹J coupling constants, comparing otherwise identical P–P and P–P(S) bonds, is 100 Hz.

³¹P{¹H} NMR spectra of α -P₄S₃(S)(SCHMeCH₂I)₂ (**2**, X = Y = (SCHMeCH₂I))

Because the P_D signals of this compound were obscured by those of other compounds in the reaction mixtures, useful computer fits to the other three multiplets of each diastereomer were not possible. The best available approximations to coupling constants were the corresponding splittings, averaged where more than one instance of the splitting was observed. The accuracy obtainable in this way was too low, compared with the small diastereomeric differences in couplings, for one of the four multiplets in each region to be assigned to the same particular diastereomer. This association also could not be made on the basis of comparisons of diastereomeric differences in chemical shifts, with corresponding differences assigned for α -P₄S₃(S)(SCHMeCH₂I)I, where these existed. Only some were similar. The four diastereomers were of approximately the same abundance, so relative peak heights gave no further information.

Phosphorus P_A gave well resolved, interleaved, eight-line multiplets for all four diastereomers. The six differences in chemical shifts included two similar pairs, assigned to diastereomeric shifts $\delta\delta$ (P_A) (1.866, 1.862, 0.209, 0.205 ppm). One pair was caused by differing chirality of the thiolate X, and the other by Y.

The P_B region consisted of two interleaved doublets ($^1J(P_AP_B)$) of quartets, where the quartet splitting was caused by near correspondence of $^2J(P_BP_C)$, $^3J(P_BP_D)$, and the smaller pair of diastereomeric shifts $\delta\delta(P_B)$. Neither coupling was available separately from other multiplets. The average value of these three splittings was 8.5 Hz at 121.5 MHz, giving 0.070 ppm for $\delta\delta$. The larger pair of diastereomeric shifts $\delta\delta(P_B)$, between the doublets of quartets, was measurable directly as 0.941 and 0.940 ppm. The observation of quartets was similar to the P_B region of α - $P_4S_3(S)(SCHMeCH_2I)$, above. The two compounds have similar values of $^3J(P_BP_D)$. This shows that the coupling is positive in the sulfurised dithiolate, as it is in α - $P_4S_3I_2$ (+9.3 Hz), so that the average value which might be predicted by our balancing rules [2] for the sulfurised thiolate iodide would approximate to the observed values (Table 1). In contrast, the coupling $^3J(P_BP_D)$ in unsulfurised α - $P_4S_3(SCHMeCH_2I)$ was almost zero, corresponding to the prediction that it should be the average of a negative coupling in α - $P_4S_3(SCHMeCH_2I)_2$ and the similar but positive coupling in the diiodide. Coupling $^3J(P_BP_D)$ in α - $P_4S_3(S)(NPr^i_2)_2$ is also positive [3], in contrast to the unsulfurised diamide.

The P_C region was complicated similarly by accidental equalities, and appeared at 121.5 MHz as a doublet ($^1J(P_CP_D)$) of triplets ($^2J(P_AP_C)$, larger $\delta\delta(P_C)$) of triplets ($^2J(P_BP_C)$, smaller $\delta\delta(P_C)$). The first triplet splitting could be resolved into a doublet ($\delta\delta(P_C)$) of doublets ($^2J(P_AP_C)$) by remeasurement at 202.5 MHz, confirming the common coupling with the P_A multiplets. The larger pair of shifts $\delta\delta(P_C)$ was 0.483 and 0.485 ppm. The second triplet splitting (average value 0.055 ppm) was not resolved at the higher frequency.

The resulting best estimates for chemical shifts of the diastereomers (in order of frequency in each region) and average couplings (over all diastereomers) were as follows. Chemical shifts: P_A 56.91, 56.70, 55.04, 54.84; P_B 161.77, 161.70, 160.83, 160.76; P_C 140.63, 140.57, 140.14, 140.08 ppm. Couplings: $^2J(P_AP_C)$ 59.9; $^1J(P_AP_B)$ -381.6; $^1J(P_CP_D)$ -285.1; $^2J(P_AP_D)$ 42.9; $^2J(P_BP_C)$ ca. 9; $^3J(P_BP_D)$ ca. 9 Hz.

As might be expected, $^1J(P_AP_B)$, $^2J(P_BP_C)$ and $\delta(P_B)$ had similar values to those in α - $P_4S_3(S)(SCHMeCH_2I)I$, and $\delta(P_A)$, though lower by 12.92 ppm, was in the same region of the spectrum. Just as $\delta(P_C)$ was much higher in the sulfurised thiolate iodide (141.45 ppm) than in the unsulfurised compound (114.67), so here it was even higher (140.36) compared with the unsulfurised dithiolate (103.61). This may show the effect of a balancing of a higher $\delta(P_C)$ with the lower value of $\delta(P_A)$, as seen for previous, unsulfurised compounds [9]. The coupling $^1J(P_CP_D)$, to the unsulfurised P_D carrying the thiolate substituent, had a similar value to that in the unsulfurised dithiolate.

Conclusions

Methylthiirane **3** does not sulfurise α - $P_4S_3I_2$ (**1**, $X = Y = I$) at 60 °C, nor at 21 °C in the presence of $Re(O)Cl_3(PPh_3)_2$, but under either conditions it will sulfurise the resulting insertion product *exo,exo*- α - $P_4S_3(SCHMeCH_2I)I$ (**1**, $X = SCHMeCH_2I$, $Y = I$), to give α - $P_4S_3(S)(SCHMeCH_2I)I$ **2**, in which the added, 1-coordinate, sulfur atom is attached to the

same phosphorus atom as the thiolate group $SCHMeCH_2I$. Under the thermal conditions, one sulfur atom was added similarly to the diinsertion product *exo,exo*- α - $P_4S_3(SCHMeCH_2I)_2$. Jason concluded that rates of addition of sulfur from Ph_3AsS , to binary phosphorus sulfides, increased with the number of bridging sulfur atoms already attached to the phosphorus to be sulfurised [15]. He expressed this in terms of the local oxidation state of this phosphorus (i.e. number of 2-coordinate sulfur ligands rather than 3-coordinate phosphorus ligands), but in the present work we show that replacing an iodide substituent by thiolate, with no change in oxidation state, also promotes sulfurisation. Two bridging sulfur atoms, S_a and S_d (Scheme 1) were insufficient to allow sulfurisation of the α - P_4S_3 cage **1** at P_A , but S_b and the sulfur of the thiolate group were sufficient for sulfurisation at P_B . Thiolate sulfur is likely to be a better π -donor to phosphorus than bridging, cage sulfur (and certainly than iodide), and it is probably the extent of π -donation which controls susceptibility to sulfurisation.

Experimental Section

All operations were carried out under nitrogen by Schlenk methods. CS_2 was dried by distillation from P_4O_{10} . α - $P_4S_3I_2$ was prepared by reaction of P_4 , S_8 , and I_2 in CS_2 [16]. Methylthiirane **3** and $Re(O)Cl_3(PPh_3)_2$ (Aldrich) were used as received. ^{31}P NMR spectra were measured in 10 mm diameter tubes at 294 K using a Bruker WM300WB spectrometer operating at 121.5 MHz, or using a Jeol Lambda 500 spectrometer at 202.5 MHz. Inverse-gated 1H decoupling was used to suppress proton coupling while avoiding the Nuclear Overhauser Effect. Precision capillaries containing $(CD_3)_2CO$ were used for locking. Chemical shifts are reported relative to H_3PO_4 -water. ^{13}C NMR spectra and DEPT measurements were obtained using the Jeol spectrometer. Ab initio calculations were carried out using Gaussian 98 [17].

Typical experiment: reaction of α - $P_4S_3I_2$ with methylthiirane in the ratio 1 : 2.

α - $P_4S_3I_2$ (0.5 g, 1.055 mmol) was dissolved in CS_2 (20 cm³), and *rac*-methylthiirane (0.165 cm³, 2.11 mmol) was added. The solution was stirred at 21 °C in the dark for 22 hours. A part (a) (10 cm³) of the clear yellow solution was treated with $Re(O)Cl_3(PPh_3)_2$ (40 mg, 0.048 mmol), to give a dark brown solution after a few minutes, which was stirred for a further 5 hours at 21 °C. The remainder (b) of the original solution was heated to reflux (bath temperature 60 °C) for 5 hours, with no change in appearance. Samples of all three solutions were analysed by NMR, as described above.

Supporting Information (see footnote on the first page of this article): rotatable ab initio molecular models as Chime/Rasmol .spt files or .xyz coordinate files; corresponding energies.

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Scheme 1. Atom labelling and enantiomer definition for α -P₄S₃ skeletons **1** and α -P₄S₃(S) skeletons **2**. Methylthiirane **3**.

Scheme 2. Proposed mechanism for insertion of methylthiirane into the P_B-I bond of α -P₄S₃I₂ (**1a**).

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