Sulfurization of Trivalent Phosphorus Compounds with 1,2-Dithiole-3-thione†

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A few methods have been utilized for the preparation of tertiary phosphine sulfides, R₃P=S.¹ These include the reaction of organometallic reagents with halides of phosphorus thioacids,² the Fridel-Crafts reaction between thiophosphonyl (thiophosphoryl or thiophosphinic) chlorides and arenes³ or between phosphorus trichloride and benzene in the presence of elemental sulfur.⁴ The most convenient preparation of such phosphine sulfides constitutes still the direct sulfurization of the parent phosphines. Here again a few reagents have been applied including elemental sulfur,⁵ sodium polysulfides⁶ and cyclic organic sulfides.⁷ Similarly, the addition of elemental sulfur to phosphites (or other trivalent analogues) constitutes the most common procedure for the preparation of the corresponding thionophosphates (or other thionoanalogues).

Earlier, one of us has reported⁸ that the reaction of 1,2-dithiolane-3-thione ¹ with triphenylphosphine ²a afforded (beside the [C₃H₂S₂]ₙ polymer terminated by Ph₃P substituent³) almost quantitative yield of the corresponding triphenylphosphine sulfide ⁴a (Eq. 1). This observation indicates a possibility of the use of the thione ¹ as a new sulfurizing reagent for trivalent organophosphorus compounds.

₄a Ar=Ph (1)

In this context, it is interesting to note that in the chemical literature one can find only two papers describing the thionation type of the reaction between phosphorus compound and a thiocarbonyl component. The first paper reported⁹ that the reaction of 4,5-dicyano-1,3-dithiole-2-thione ⁵ with tri-n-butylphosphine ²b gave a mixture of products, one of which was identified as tri-n-butylphosphine sulfide ⁴b (Eq. 2). The second one described¹⁰ the high temperature (100 °C) reaction of tri-n-butylphosphine ²b with thiobenzophenone ⁶ which gave mainly tri-n-butylphosphine sulfide ⁴b (89%), 1,1,2,2-tetraphenylethane ⁷ (65%) and tetraphenylethylene (28%) (Eq. 3). The intermediacy of carbene in the reaction was suggested.

₄b Ar=Ph (2)

Results and Discussion

To show a possibility of application of the thione ¹ as a new sulfurizing reagent we have started our experiments with a few trialkyl phosphites ⁹. We were glad to find that in this case sulfurization reaction is rapid and very clean giving at room temperature the corresponding thionophosphates ¹⁰ as a single reaction product (³¹P-NMR assay) (Eq. 4). On the other hand, under the same reaction conditions triphenylphosphite ⁹d (R=Ph) gave a complex mixture of phosphorus-containing products.

₄d Ar=Ph (3)

In a sharp contrast to this when a few aromatic and aliphatic tertiary phosphines ²a-g were allowed to react with the thione ¹ in boiling benzene for a few hours the corresponding phosphine sulfides ⁴a-g were formed cleanly although always accompanied by the traces of the corresponding phosphine oxides (³¹P-NMR assay). They were isolated in a very high yield (Table 1) by a standard column chromatography of a crude reaction product.

If the reaction of P³⁺ compounds with 1,2-dithiole-3-
thione 1 were found to be stereospecific, this thione would be the preferred reagent for thionation of chiral phosphines. With this in mind we have examined thionation of optically active (+)-(S)-methyl-n-propylphenyl phosphine 11 and found that it resulted in the formation of the corresponding (+)-(R)-phosphine sulfide 12 with stereoselectivity close to 70% and with retention of configuration at phosphorus (Eq. 5).

On the other hand, the reaction between the levorotatory phosphine oxide (−)-(S)-13 and the thione 1 gave after 33 days at room temperature the dextrorotatory enantiomer of t-butylphenylphosphinothioic acid (+)-(R)-14 with full retention of configuration at the stereogenic phosphorus atom (Eq. 6). However, a few unidentified phosphorus-containing products having chemical shifts around +70 ppm were observed in a crude reaction mixture (31P-NMR assay).

Retention at phosphorus observed in the above mentioned thionation reactions may be easily explained by the mechanistic sequence proposed in Scheme 1. It is reasonable to assume that the first step of the reaction between phosphines 2 or the trivalent tautomer of the phosphine oxide 13 and 1 is the nucleophilic attack of phosphorus at the 5-position of the thione as this position easily undergoes nucleophilic attack. This results in the formation of the “Zwitterion” 15. It may then undergo internal opening to give subsequently the structures 16 and 17 which upon cyclization forms the intermediate phosphorane 18, in which the five membered ring spans axial and equatorial positions. Such a structure should be the most convenient from the point of view of apicophilicity of substituents at phosphorus in trigonal-bipyramidal species. Decomposition of the five-coordinate intermediate 18 gives the phosphine sulfide with retention of configuration at phosphorus and the carbene intermediate 19 from which polymer 20 could possibly be formed. This proposal is in full agreement with the experimental observation that a black polymeric precipitate was always formed during the discussed thionation reaction.

Experimental Section

General. Melting points which are uncorrected were

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Yield [%]</th>
<th>Mp [°C]</th>
<th>31P-NMR CDCl3/85%H3PO4</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a Ph</td>
<td>83</td>
<td>158-160</td>
<td>157-158°</td>
</tr>
<tr>
<td>2b n-Bu</td>
<td>86</td>
<td>oil</td>
<td>134-136/0 mmHg17</td>
</tr>
<tr>
<td>2c p-Tol</td>
<td>87</td>
<td>181-183</td>
<td>185-186°</td>
</tr>
<tr>
<td>2d p-Cl-C6H4</td>
<td>83</td>
<td>149-151</td>
<td>152-153°</td>
</tr>
<tr>
<td>2e p-F-C6H4</td>
<td>86</td>
<td>137-138</td>
<td>139-141°</td>
</tr>
<tr>
<td>2f p-MeO-C6H4</td>
<td>90</td>
<td>107-110</td>
<td>109-110°</td>
</tr>
</tbody>
</table>

*isolated after column chromatography
determined in capillary tubes. $^{31}$P NMR spectra were obtained on a Burker 200 MHz and JOEL 400 MHz spectrometer and the $^{31}$P chemical shifts are reported as referenced to the external 85% H$_3$PO$_4$ with resonance deshielded from the reference as being reported as positive. Thin layer chromatograms for analytical purposes were run on alumina plates coated with a layer of silica gel GF$_{254}$ (Merck). Column chromatography was done on silica gel (Merck, 60-200 mesh). Optical activity measurements were made with a Perkin-Elmer 241 MC photopolarimeter: concentrations of the solutions were about 1-2 g/100 mL.

Materials. All starting trialkyl(aryl) phosphates and triarylphosphines were commercially available products. 1,3-Dithiole-3-thione,$^{16}$ (+)-(S)-methyl-$n$-propylphenylphosphine$^{13}$ and (-)-(S)-butylphenylphosphinothioic acid$^{14}$ by Means of Phosphorus Sulfide$^{12}$ by Means of S$.^{11}$

Reactions of 1,2-Dithiole-3-thione with TriarylpHosphines. A solution of 1,3-dithiole-3-thione (0.536 g, 0.004 mol) and triarylphosphine 2 (0.004 mol) in 50 mL of dry benzene was refluxed and the reaction progress was monitored by TLC. After cooling, the black precipitate was filtered and washed with 50 mL of ether and 30 mL of benzene. Evaporation of the benzene and the solvent used to wash the precipitate afforded a solid which was purified by column chromatography to give virtually pure products listed in Table 1.

Conversion of (+)-(S)-Methylphenyl-$n$-propylphosphine-11 to (+)-(R)-Phosphine Sulfide-12 by Means of (+)-Phosphine Sulfide-13 by Means of 1,2-Dithiole-3-thione-1.$^{16}$ A solution of 11 [448 mg (0.00024 mol), $[\alpha]_{589} =$ +18.3 (toluene), ee = 93.5%] and 1 [19 mg (0.00019 mol)] in benzene (2 mL) was stirred at room temperature for 0.5 h. After this time the black precipitate was filtered and washed with diethyl ether (3 x 20 mL). The organic phase was washed in a row with 5% aqueous solutions of H$_2$SO$_4$, 5% aqueous solution of K$_2$CO$_3$ and water and dried over dry MgSO$_4$. Evaporation of the solvent afforded a solid (39.8 mg 92%) which was purified by preparative TLC chromatography [ethyl ether-petroleum ether (1 : 1) as an eluent] to give virtually pure (+)-(R)-methylphenyl-$n$-propylphosphine sulfide 12 [21.8 mg (0.00011 mol), (46%), $[\alpha]_{589} =$ +14.4 (1.09 MeOH), ee = 63.4%, $\delta_{31\text{P}} = +41.4$ (MeOH)].

Conversion of (-)-(S)-Butylphenylphosphine Oxide-13 to (+)-(R)-Butylphenylthiophosphinic acid-14 by Means of 1,2-Dithiole-3-thione-1.$^{13a}$ A solution of 13 [0.184 g (0.001 mol), $[\alpha]_{589} =$ −32.5 (1.53 CHCl$_3$), ee = 88.4%] and 1 [80 mg (0.0006 mol)] in CDCl$_3$ (2 mL) was kept in a NMR tube at room temperature for 33 days and the reaction progress was followed by the $^{31}$P NMR. After this time the black precipitate was filtered and washed with diethyl ether (3 x 20 mL). Evaporation of the CDCl$_3$ and the solvent used to wash the precipitate afforded a solid which was purified by column chromatography [ethyl ether-petroleum ether (1 : 1) as an eluent] to give (+)-(R)-butylphenylthiophosphinic acid 14 [0.092 g (48%), $[\alpha]_{589} =$ +26.4 (1.06 MeOH), ee = 88.4%, $\delta_{31\text{P}} = +98.6$ (CDCl$_3$)].

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References
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