

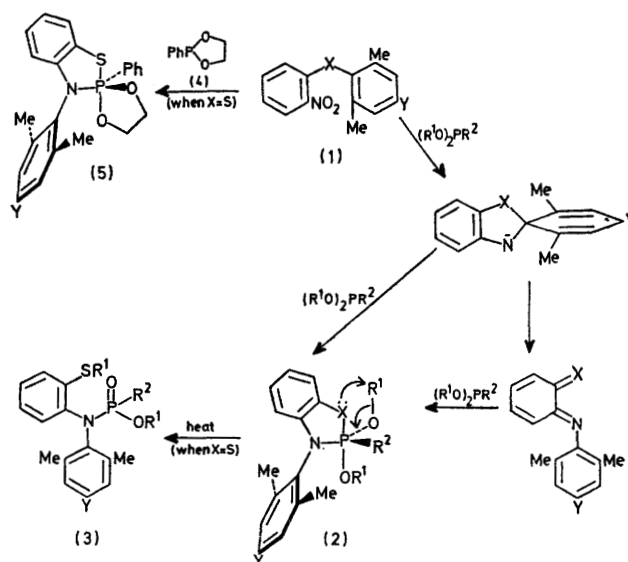
3-Aryl-2,3-dihydro-1,3,2-benzothiazaphosph(v)oles. A New Class of Phosphoranes

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Summary Aryl 2-nitrophenyl sulphides react with trivalent phosphorus reagents to give the novel oxythiazaphosphoranes (**2**; X = S) which easily isomerise to the phosphoramidates (**3**), except in the case of the more stable bicyclic analogues, *e.g.*, 3-(2,6-dimethylphenyl)-2,2-ethylenedioxy-2-phenyl-2,3-dihydro-1,3,2-benzothiazaphosph(v)ole (**5**; Y = H), which, by X-ray crystallography, is much distorted towards a square pyramid.

WHEREAS reactions of aryl 2-nitrophenyl ethers (**1**; X = O) with $(R^1O)_2PR^2$ give high yields of oxazaphosphoranes (**2**; X = O),¹ the corresponding thiazaphosphoranes (**2**; X = S) were not isolated or detected in the analogous reactions of aryl 2-nitrophenyl sulphides² (**1**; X = S); the only phosphorus-containing products were phosphoramidates² (**3**). A possible explanation of this marked difference is that these reactions of (**1**; X = O or S) had both proceeded in the same way to give phosphoranes, except that when X = S, the first formed thiazaphosphorane (**2**; X = S), by virtue of the higher nucleophilicity to saturated carbon of sulphur compared with oxygen,³ had isomerised to the observed phosphoramidate (**3**).



We now report experimental verification of this by detection and, in some cases, isolation of the elusive 3-aryl-2,3-dihydrobenzothiazaphosph(v)oles (**2**; X = S), a novel class of thiazaphosphoranes.

TABLE. Bond angles ($^{\circ}$) and distances (\AA) around phosphorus in (**5**; Y = H).

| Angle | Found | Ideal sq. pyramidal | Ideal trigonal bipyramidal |
|-------------|-------|------------------------|----------------------------------|
| S-P-O(1) | 163 | 150 | 180 |
| S-P-O(2) | 81 | 86 | 90 |
| S-P-N | 89 | 86 | 90 |
| S-P-C | 99 | 105 | 90 |
| O(1)-P-O(2) | 91 | 86 | 90 |
| O(1)-P-N | 88 | 86 | 90 |
| O(1)-P-C | 97 | 105 | 90 |
| O(2)-P-N | 139 | 150 | 120 |
| O(2)-P-C | 109 | 105 | 120 |
| N-P-C | 112 | 105 | 120 |

Distances; P-S 2.187; P-O(1) 1.65; P-O(2) 1.63; P-N 1.72 P-C 1.81 \AA .

Thus, while the sulphide (**1**; X = S, Y = H) (2.5 mmol) and $(\text{MeO})_3\text{P}$ (15 mmol) in an excess of cumene after 90 h at 130°C gave an almost quantitative yield of the phosphoramidate (**3**; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{OMe}$, Y = H), ^{31}P n.m.r. spectroscopy revealed a peak at $\delta +23.98$ p.p.m. indicative of a phosphorane, which with time reached a maximum (after 31 h) and then was replaced by that due to the phosphoramidate ($\delta -5.62$ p.p.m.). Similar results were obtained from reactions of the sulphides (**1**; X = S, Y = Me) with $(\text{MeO})_2\text{PPh}$ and $(\text{MeO})_3\text{P}$. Attempted isolation of the thiazaphosphorane (**2**; X = S, $\text{R}^1 = \text{Y} = \text{Me}$, $\text{R}^2 = \text{OMe}$) in the latter case led to mixtures of the phosphoramidate (**3**; $\text{R}^1 = \text{Y} = \text{Me}$, $\text{R}^2 = \text{OMe}$) and the phosphorane, as shown by ^{31}P and ^1H n.m.r. spectroscopy. After neglect of the signals due to the isolable phosphoramidate (**3**; $\text{R}^1 = \text{Y} = \text{Me}$, $\text{R}^2 = \text{OMe}$), those of the phosphorane (**2**; $\text{R}^1 = \text{Y} = \text{Me}$, $\text{R}^2 = \text{OMe}$, X = S) were identifiable: δ 2.07 (2Me, s), 2.35 (Me, s), 3.53 ($3 \times \text{Me-O-P}$, d, J 15 Hz), 5.8 (1H, m, ArH), and 6.5–7.4 (5H, m, ArH). This thiazaphosphorane was too easily isomerised into the phosphoramidate to be isolated by distillation or crystallisation but use of the cyclic tervalent phosphorus reagent, 2-phenyl-1,3,2-dioxaphospholan (**4**) with the sulphides (**1**; X = S; Y = Me or H) led to the isolation of the corresponding thiazaphosphoranes (**5**; Y = Me or H); their greater stability being in accord with their bicyclic structures. The reaction is exemplified by the isolation of the spiro-compound (**5**; Y = H, 73%), m.p. 162–164.5 $^{\circ}\text{C}$, b.p. 218–227 $^{\circ}\text{C}$ at 0.05 mmHg; ^{31}P n.m.r. spectrum $\delta +10.62$ p.p.m., correct analysis and mass spectrum. The structure (Figure) determined by X-ray crystallography confirms this assignment.

Crystal data: Monoclinic, space group $P2_1/c$; $a = 10.35$, $b = 9.74$, $c = 19.21$ \AA , $\beta = 96.5^{\circ}$, $Z = 4$. 1959 independent intensities were measured. The structure was solved using the MULTAN system.⁴ The phosphorus co-ordination and important bond angles and bond distances are given in the Table. Other bonds and angles have normal values.

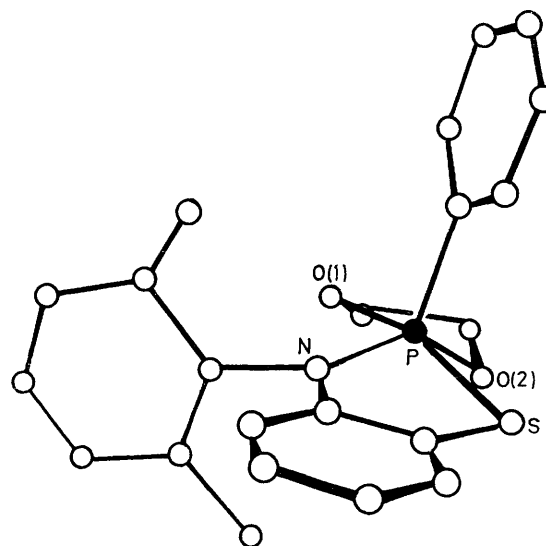


FIGURE. One molecule projected along a^* . Hydrogen atoms are omitted. Unlabelled atoms represent carbon.

These results are of interest not only for the isolation of the first examples of the novel thiazaphosphoranes and for the mechanistic unity which they impart to deoxygenation reactions of both the ethers and sulphides (**1**; X = O or S), but also because they provide further examples of the rare departure from trigonal bipyramidal geometry of phosphoranes.⁵ The Table shows that considerable distortion towards a square pyramid exists in (**5**; Y = H). Alternatively, if it is preferred to consider that (**5**; Y = H) is a much distorted trigonal bipyramid it is of interest that the sulphur ligand is apical while the nitrogen is equatorial in accord with expectation,⁶ and that the pendant *N*-aryl ring is orthogonal to the second, fused, benzene ring in accord with the configuration of the analogous oxyphosphoranes.^{2a,7}

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