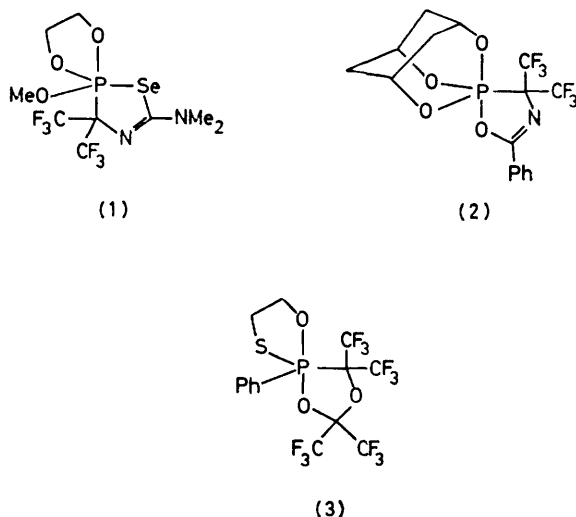


## The Apicophilicity of the Phenylseleno Group in Five-co-ordinate Phosphoranes

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The variable-temperature n.m.r. spectra of spirophosphoranes containing a *P*-phenylseleno group show that in these systems phenylseleno, phenylthio, and phenoxy groups possess similar apicophilicities. In the case of a spirophosphorane containing a benzoxathiaphosphole ring there is no evidence in solution of an isomer with apical sulphur, *i.e.* there is here a substantial difference in apicophilicity between oxygen and sulphur which is not apparent with phenoxy and phenylthio groups.

THE first five-co-ordinate selenophosphorane (1) was reported by Burger;<sup>1</sup> surprisingly the structure, as established by *X*-ray analysis, consisted of a distorted trigonal bipyramid with equatorial selenium and apical carbon bearing two trifluoromethyl groups. Comparison with structures (2)<sup>2</sup> and (3),<sup>3</sup> in which apical oxygen is



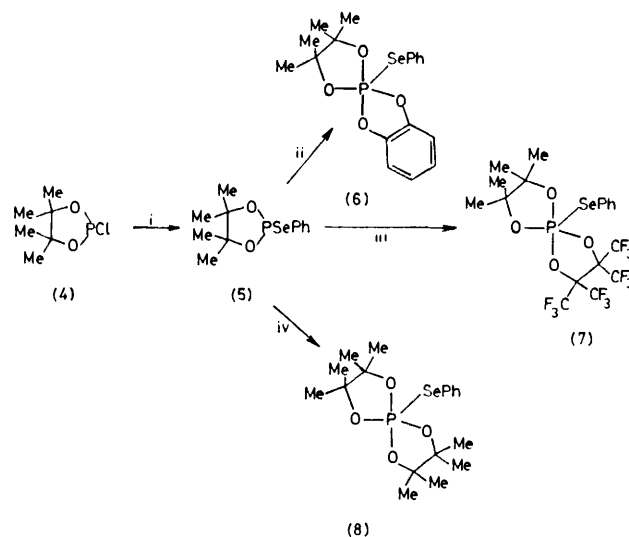
preferred over similar carbon, suggests that selenium is less apicophilic than oxygen, or by extension,<sup>4</sup> sulphur. We have made a number of five-co-ordinate phosphoranes containing a *P*-phenylseleno group in order to investigate this point.

Reaction of the chlorophosphonite (4) with lithium phenyl selenide gave the selenophosphite (5), which could not be distilled. From it were prepared the crystalline phosphoranes (6)–(8) (Scheme).

At room temperature the <sup>1</sup>H n.m.r. spectrum of (6) in 1-bromonaphthalene showed two methyl signals of equal intensity; these coalesced reversibly at 115 ± 2 °C as the pseudorotation (6) ⇌ (9) became rapid on the n.m.r. time-scale; the free energy of activation for this process is therefore 21.1 ± 0.1 kcal mol<sup>-1</sup>.† Comparison with the values<sup>4</sup> of 20.5 and 20.7 kcal mol<sup>-1</sup> for the corresponding pseudorotations of the analogous phenoxy and phenylthio phosphoranes, respectively, suggests that in this system the phenylseleno group is slightly less

† 1 cal = 4.184 J.

apicophilic than phenoxy or phenylthio. The two signals in the <sup>19</sup>F n.m.r. spectrum of (7) similarly coalesced at 185 ± 5 °C (Δν 130 Hz in 1-bromonaphthalene), and the free energy of activation for the pseudorotation (7) ⇌ (10) is therefore 22.1 ± 0.3 kcal mol<sup>-1</sup>. The value<sup>4</sup> for the corresponding phenylthiophosphorane is 22.3 kcal mol<sup>-1</sup>; the phenoxy-

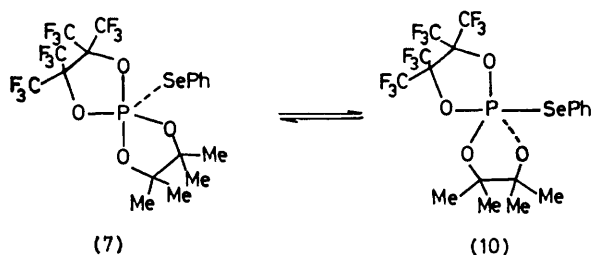
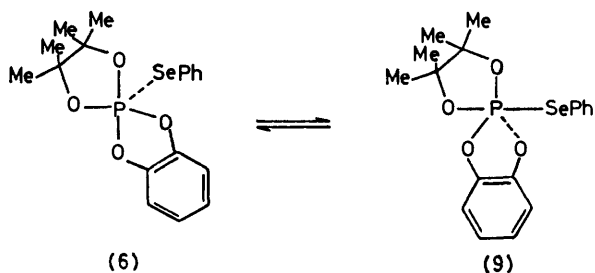


SCHEME Reagents: i, PhSeLi; ii, Pr<sub>2</sub>NCl, catechol; iii, (CF<sub>3</sub>)<sub>2</sub>CO; iv, Pr<sub>2</sub>NCl, pinacol

phosphorane showed adventitious equivalence of the trifluoromethyl groups. In this system phenylseleno and phenylthio groups therefore have similar apicophilicities. The phosphorane (8) decomposed before coalescence of the two methyl signals in its proton n.m.r. spectrum.

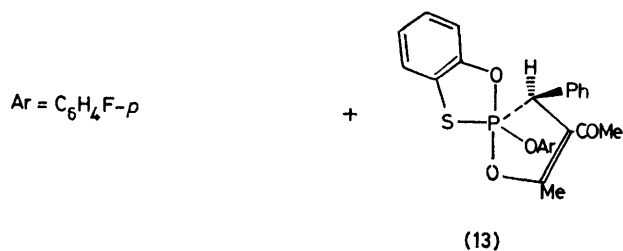
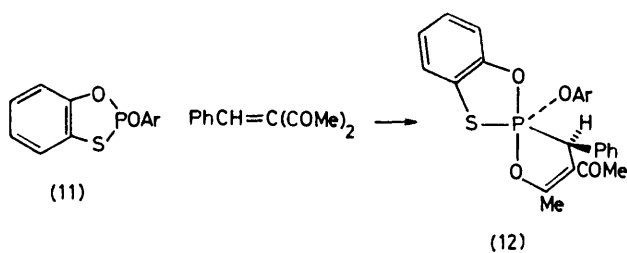
These results are surprising in view of the structure of the selenophosphorane (1). However, the structure of (3), with apical oxygen and equatorial sulphur, is also noteworthy in view of the similar apicophilicities of ethoxy and ethylthio groups,<sup>5</sup> and the possibility arises that placing heteroatoms in rings changes their relative apicophilicities. That this can be the case was shown by a study of the *trans*-phosphorane (12) formed by the addition of 3-benzylidenepentane-2,4-dione to the thiophosphite (11). If, by analogy with phenoxy and phenylthio,<sup>4</sup> the oxygen and sulphur atoms in this *trans*-

phosphorane have similar apicophilicities, then it should exist in solution as the isomers (12) and (14), having oxygen or sulphur apical, respectively. These isomers can interconvert by the pseudorotation process shown, which should have <sup>6</sup> a free energy of activation of about 15 kcal mol<sup>-1</sup>, whereas interconversion of *trans*- (12)

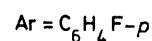
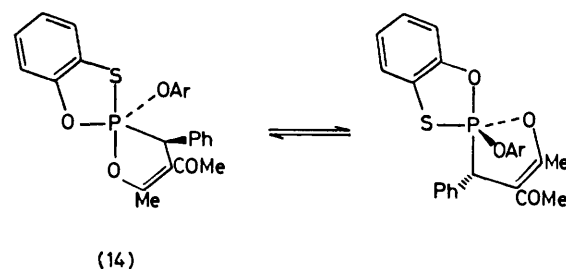
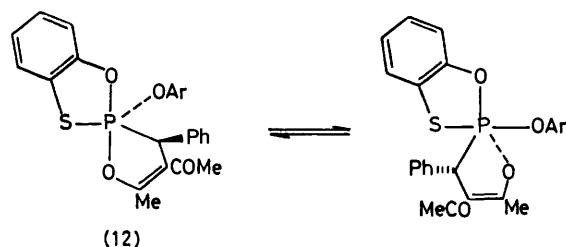


and *cis*- (13) isomers, which requires placing the benzoxathiaphosphole ring diequatorial, is slow at room temperature even on a normal kinetic time-scale.

The isomers (12) and (13) were prepared as a mixture (3 : 1) and the *trans*-isomer (12) was obtained pure by careful crystallisation. X-Ray analysis<sup>7</sup> showed it to be a slightly distorted trigonal bipyramid with equatorial sulphur and the *trans* configuration as shown in (12). In solution at room temperature it is slowly converted into the 3 : 1 equilibrium mixture as shown by <sup>31</sup>P n.m.r. spectroscopy.



When the pure isomer (12) was dissolved in dichloromethane at  $-70^\circ\text{C}$ , the <sup>31</sup>P n.m.r. spectrum of the solution at this temperature showed only one doublet ( $J_{\text{PF}}$  4.4 Hz), due to (12). On brief warming to room temperature and recooling to  $-70^\circ\text{C}$  the same <sup>31</sup>P n.m.r. spectrum was observed. Repetition of this process eventually led to the appearance of a new doublet due to the *cis*-isomer (13), but no other new signals. The pseudorotation (12)  $\rightleftharpoons$  (14) is slow on the n.m.r. time-scale at



$-70^\circ\text{C}$  but rapid on the kinetic time-scale at room temperature; the lack of any signals ascribable to (14) in the above sequence shows that the equilibrium between (12) and (14) is overwhelmingly on the side of (12), *i.e.* in this phosphorane oxygen is at least 2 kcal mol<sup>-1</sup> more apicophilic than sulphur.

The origin of this change in the relative apicophilicities of oxygen and sulphur when they are both constrained in a ring is not known; it could be related to changes in hybridisation or to the restriction of lone-pair orientations.

At low temperatures one of the two signals in the <sup>19</sup>F n.m.r. spectrum of the spiroposphorane (7) splits into two equal signals ( $T_c -55 \pm 1^\circ\text{C}$ ,  $\Delta\nu$  208 Hz;  $\Delta G^*$  10.0  $\pm$  0.1 kcal mol<sup>-1</sup>); this is probably associated with slowing of rotation round the equatorial P-Se bond. A similar phenomenon has been observed previously with the corresponding phenylthiophosphorane.<sup>8</sup> The <sup>31</sup>P n.m.r. spectra of compounds containing a P-Se bond show satellite peaks due to <sup>31</sup>P-<sup>77</sup>Se spin-spin coupling from the 7.5% natural abundance of <sup>77</sup>Se. The  $J_{\text{PSe}}$  value for the selenophosphite (5) was 342 Hz, whereas for the five-co-ordinate phosphoranes it ranged from 459 to 620 Hz; as with other electropositive elements attached

to phosphorus there is therefore a tendency for this single bond coupling to increase with the s-character of the phosphorus orbital.<sup>9</sup>

#### EXPERIMENTAL

N.m.r. spectra (<sup>31</sup>P and <sup>19</sup>F) were recorded for solutions in CH<sub>2</sub>Cl<sub>2</sub> unless otherwise stated; positive chemical shifts are to low field of the standards 85% H<sub>3</sub>PO<sub>4</sub> and C<sub>6</sub>H<sub>5</sub>CF<sub>3</sub>, respectively. Free energies of activation at the coalescence temperatures were calculated using the Gutowsky-Holm equation. Light petroleum refers to the fraction having b.p. 60–80 °C.

**4',4',5',5'-Tetramethyl-P-phenylseleno-1,3,2-benzodioxaphosphole-2-spiro-2'-(1',3',2'-dioxaphospholan) (6).**—Lithium triethylhydridoborate [1M in tetrahydrofuran (THF)] was slowly added to a stirred solution of diphenyl diselenide (1.56 g) in THF (15 ml) until the bright yellow colour disappeared.

2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (1.82 g) was then added and the solution set aside at room temperature for 3 h. The resulting 4,4,5,5-tetramethyl-2-phenylseleno-1,3,2-dioxaphospholan,  $\delta_P$  228.1 ( $J_{PSe}$  342 Hz), was used without isolation.

N-Chlorodi-isopropylamine (1.4 g) in ether (20 ml) was added slowly with stirring to the above phospholan and catechol (1.1 g) in ether (20 ml) at –78 °C and the mixture set aside at room temperature for 24 h. Filtration and evaporation then gave the *phosphorane* (6), m.p. (from light petroleum) 124 °C;  $\delta_H$  1.20 (6 H, s), 1.30 (6 H, s), 6.6 (4 H, br, s), 7.05 (3 H, m), and 7.45 (2 H, m);  $\delta_P$  –20.4 (Found: C, 52.7; H, 5.15; P, 6.95. C<sub>18</sub>H<sub>21</sub>O<sub>4</sub>PSe requires C, 52.55; H, 5.15; P, 7.55%).

**2,2,3,3-Tetramethyl-5-phenylseleno-7,7,8,8-tetrakis(trifluoromethyl)-1,4,6,9-tetraoxa-5-phosphaspiro[4,4]nonane (7).**—The 2-phenylselenophospholan (6) (from 0.98 g of 2-chlorophospholan) was dissolved in ether (15 ml) and an excess of hexafluoroacetone was condensed into the stirred solution at –78 °C. The solution was then allowed to reflux under a solid CO<sub>2</sub>-acetone condenser for 3 h. Evaporation then gave the *phosphorane* (7), m.p. (from light petroleum) 102–103 °C;  $\delta_H$  1.05 (6 H, s), 1.25 (6 H, s), 7.1–7.8 (5 H, m);  $\delta_F$  (in 1-bromonaphthalene) –1.6 (6 F, m) and –2.8 (6 F, m);  $\delta_P$  –22.0 ( $J_{PSe}$  620 Hz) (Found: C, 34.2; H, 2.7; P, 5.05. C<sub>18</sub>H<sub>17</sub>F<sub>12</sub>O<sub>4</sub>PSe requires C, 34.05; H, 2.7; P, 4.85%).

**2,2,3,3,7,7,8,8-Octamethyl-5-phenylseleno-1,4,6,9-tetraoxa-5-phosphaspiro[4,4]nonane (8).**—N-Chlorodi-isopropylamine (1.46 g) in ether (15 ml) was added slowly to the 2-phenylselenophospholan (7) (from 1.97 g of 2-chlorophospholan) and pinacol (1.27 g) in ether (20 ml) at –78 °C and the mixture set aside at room temperature for 48 h. Filtration and evaporation then gave the *phosphorane* (8), m.p. (from light petroleum) 112–113 °C;  $\delta_H$  1.05 (12 H, s), 1.25 (12 H, s), 7.15 (3 H, m), and 7.65 (2 H, m);  $\delta_P$  –30.3 ( $J_{PSe}$  459 Hz) (Found: C, 51.75; H, 7.0; P, 7.25. C<sub>18</sub>H<sub>29</sub>O<sub>4</sub>PSe requires C, 51.55; H, 6.95; P, 7.4%).

**4'-Acetyl-r-P-(p-fluorophenoxy)-5'-methyl-t-3'-phenyl-1,3,2-benzoxathiaphosphole-2-spiro-2'-Δ<sup>4</sup>-1',2'-oxaphospholene (12).**—A solution of 2-*p*-fluorophenoxy-1,3,2-benzoxathiaphosphole (0.5 g) and 3-benzylidenepentane-2,4-dione (0.34 g) in dichloromethane (10 ml) was set aside at room temperature for 3 weeks. Evaporation and crystallisation from dichloromethane-light petroleum gave the *trans*-phosphorane (12), m.p. 125–129 °C;  $\delta_P$  13.5;  $\delta_F$  –53.8;  $\delta_H$  2.0 (3 H, s), 2.25 (3 H, s), 4.65 (1 H, d,  $J$  24 Hz), and 6.4–7.45 (13 H, m). Satisfactory elemental analyses could not be obtained for this extremely hygroscopic compound.

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