

Phosphorus–Selenium Heterocycles

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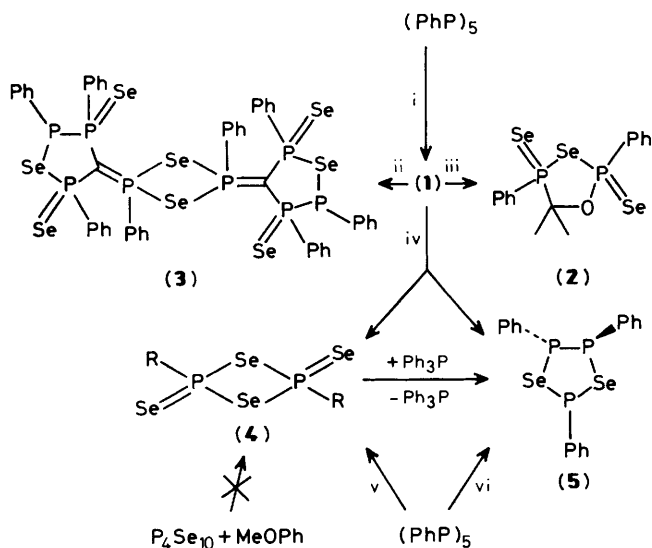
The synthesis of the first examples of four and five membered phosphorus–selenium ring compounds $\text{PhP}(\text{Se})\text{Se}_2\text{P}(\text{Se})\text{Ph}$ (a selenium analogue of Lawesson's reagent) and $(\text{PhP})_3\text{Se}_2$ via a number of routes is described, the new compounds being characterised by mass spectrometry, ^{31}P , and ^{77}Se n.m.r.

Currently we are investigating routes to phosphorus–selenium heterocycles.¹ Simple 3-membered phosphorus–selenium rings have been reported^{2–4} and we have recently prepared two new organo-phosphorus–selenium heterocycles.¹ However, no larger ring compounds are known and the preparation of a selenium analogue of Lawesson's reagent,

with potential in organic synthesis, is a particularly important goal. Attempts by Guziec *et al.*⁵ to prepare $(\text{MeOC}_6\text{H}_4)\text{P}(\text{Se})\text{Se}_2\text{P}(\text{Se})(\text{H}_4\text{C}_6\text{OMe})$ by reaction of P_4Se_{10} with anisole in an analogous fashion to the synthesis of Lawesson's reagent have failed, and in any case would require the preparation of P_4Se_{10} which is rather laborious. Here, we report on the facile synthesis of new 4- and 5-membered P–Se heterocycles from readily available starting materials.

Scheme 1 illustrates the structures of the known organo-

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Scheme 1. Reagents and conditions: i, 5 Se; ii, CS₂; iii, Me₂CO; iv, stand overnight; v, 10 Se; vi, 10/3 Se.

Table 1. ³¹P-¹H and ⁷⁷Se-¹H N.m.r. parameters for (PhP)₃Se₂ (5). Spectra are referenced against 85% H₃PO₄ and H₂SeO₃ (δ = 1282 relative to Me₂Se = 0 p.p.m.) respectively.

	δ/p.p.m.	P _A	P _B	P _X	Se _A	Se _B
P _A	92.3	—	299	41	295	13
P _B	107.6	299	—	84	18	305
P _X	120.3	41	84	—	260	267
Se _A	437	295	18	260	—	—
Se _B	451	13	305	267	—	—

phosphorus-selenium heterocycles together with the new inorganic heterocycles[‡] that we have isolated from the reactive intermediate (1). Thus, reaction of (PhP)₅ with selenium in toluene gives (1) which we have been unable to isolate or fully characterise. On standing a solution of (1) under argon overnight, (4) is precipitated as dark red microcrystals. Compound (4) may be filtered off and after addition of ether the remaining solution cooled to give (5) as yellow needles. Scheme 1 illustrates other routes which also yield (4) and (5). For example, reaction of (PhPS)₃⁶ with selenium gives (4), which is deselenated with triphenylphosphine to give (5). Additionally, (4) and (5) can be prepared from the appropriate simple stoichiometric reaction of grey selenium with (PhP)₅ in toluene.

Characterisation of (4) and (5) was achieved by microanalyses, n.m.r., vibrational spectroscopy, and mass spectrometry. The composition of the compounds comes directly from microanalytical data. Compound (4) has a mass spectrum with a parent at M⁺ (534) with the expected isotopic distribution. In its vibrational spectrum the ν(P=Se) vibration is observed at 508 cm⁻¹. In the mass spectrum of (5) although the appropriate M⁺ ion (454) is observed there is also some rearrangement to give (4). However the synthesis of (5) from (4) and PPh₃ requires 8/3 equivalents of the latter and supports our formulation. The ³¹P-¹H n.m.r. spectrum of (5) is an ABB' spectrum (at 101 MHz) and consists of three doublets of doublets with satellites due to ⁷⁷Se-³¹P couplings (Figure 1,

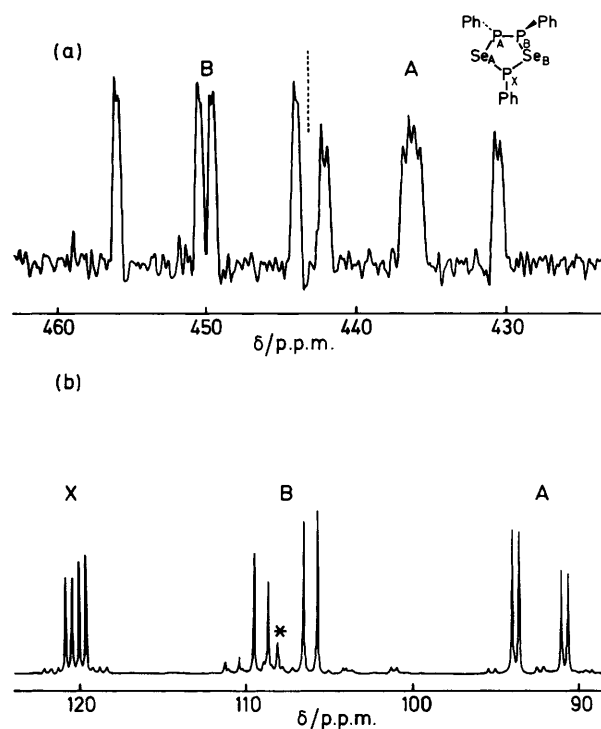


Figure 1. (a) ⁷⁷Se-¹H and (b) ³¹P-¹H N.m.r. spectra of (5). The peak asterisked in (b) is an impurity.

Table 1). This was further confirmed by measurement of a COSY spectrum. In the ³¹P n.m.r. there is one large and two small ³¹P-³¹P couplings leading to the conclusion that two phosphorus atoms are directly bonded with the third phosphorus being more distant. The ⁷⁷Se-n.m.r. spectrum (Figure 1, Table 1) consists of two doublets of doublets of doublets. For (5) we observed no band due to ν(P=Se) in the i.r. or Raman and the ⁷⁷Se-³¹P coupling constants are substantially lower than those seen for P=Se (ca. 700 Hz⁷) and a cyclic structure is thus reasonable. The structure of (4) has an analogue in sulphur chemistry, i.e. the well known Lawesson's reagent, whereas the structure of (5) has no analogues in sulphur chemistry but is isoelectronic with the starting material (PhP)₅ and related to the five-membered heterocycle which has one exocyclic P=S group, (PhPS)₃.⁸

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[‡] All new compounds gave satisfactory microanalyses.