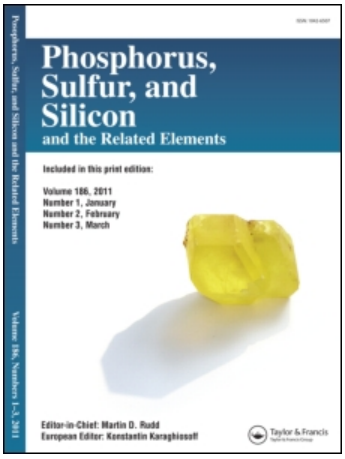

Phosphorus, Sulfur, and Silicon and the Related Elements

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New Phosphorus-Selenium Heterdcycles

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NEW PHOSPHORUS-SELENIUM HETEROCYCLES

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Abstract The preparation of new phosphorus-sulphur and phosphorus-selenium heterocycles is described. The new compounds have been characterised by multinuclear NMR (^{31}P, ^{77}Se) and X-ray crystallography.

The chemistry of phosphorus-sulphur and phosphorus-selenium cages is quite well developed. P_4S_3 is used in the manufacture of "strike anywhere" matches whilst P_4S_{10} is used in the preparation of lubricant additives and as a reagent in organic synthesis. During the past two years we have become interested in the preparation of new P-S and P-Se systems for a number of reasons. Apart from the intrinsic interest in defining the limits of what compounds may be synthesised new ring systems may be valuable as reagents for the conversion of ketones into thio or seleno-ketones. The most well developed chemistry in this area uses Lawessons reagent which is commercially available. Here we describe our work in the synthesis of new P-S[2] and P-Se[3,4] rings related to Lawessons reagent.

Reaction of P_4S_3 with S_8 in α-bromonaphthalene at 240°C is reported[1] to give P_4S_9 in moderate yield. However we have found that the reaction is very sensitive to the conditions used. In order to maximise yields of P_4S_9 a slightly lower

temperature (220°C) is better. Furthermore, if the temperature is raised above 240°C the new heterocycle (1) (Figure 1) is obtained[2]. The x-ray structure of (1) reveals that the P_2S_2 ring is puckered with a dihedral angle of 135° about the S...S' axis. The transannular S...S distance is 3.05 Å. (1) reacts with benzophenone and triphenylphosphine oxide to give the corresponding sulphide indicating its potential as a thionating agent.

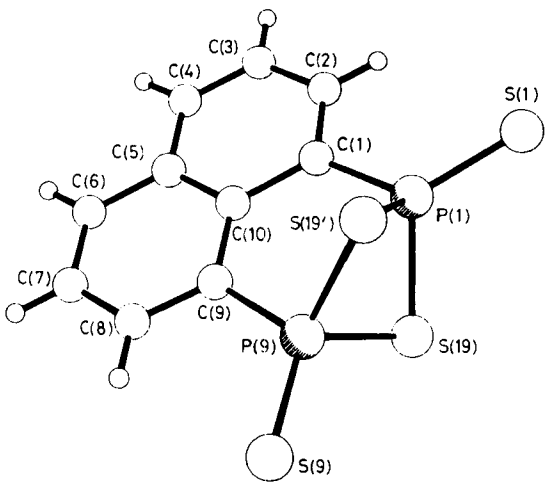


FIGURE 1 The X-ray crystal structure of (1).

In view of the formation of (1) we investigated routes to new P-Se heterocycles. Reaction of grey selenium with $(PhP)_5$ in refluxing toluene proceeds smoothly with the selenium being dissolved in a matter of minutes. If this reaction mixture is allowed to cool overnight a deep red selenium analogue (2) of Lawessons reagent is deposited[4]. Unfortunately, we have been unable to obtain crystals suitable for X-ray analysis.

However, the mass spectrum, IR and microanalyses strongly support our proposed structure. The solution from the above reaction can be reduced in volume to give a second P-Se heterocycle, (3), as yellow needles. The ^{77}Se and ^{31}P NMR spectra of (3) are shown in Figure 2. The ^{31}P spectrum consists of three doublets of doublets, each with selenium satelites whilst the ^{77}Se spectrum consists of two doublet of doublet of doublets. This data together with the mass spectral and vibrational spectral data allows for unequivocal structural characterisation of (3)[4].

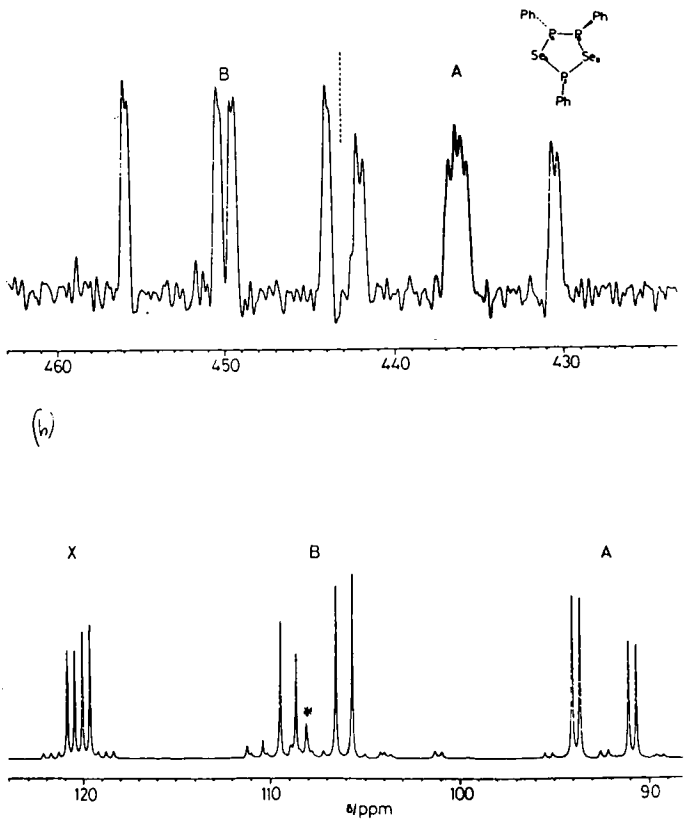
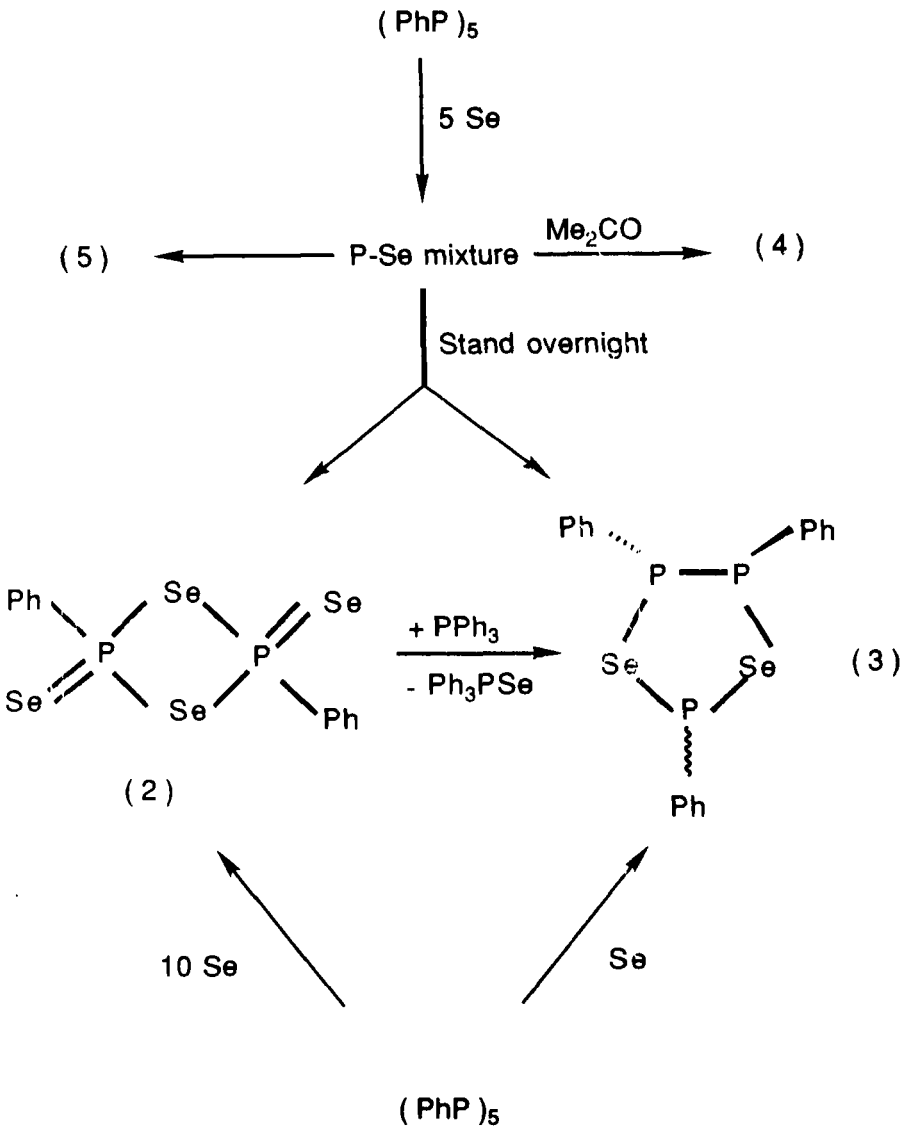


FIGURE 2 ^{77}Se (upper) and ^{31}P NMR (lower) spectra of (3).

If rather than cooling the reaction mixture described above overnight it is treated with acetone or carbon disulphide two new heterocycles [(4) & (5)] can be isolated[3]. The overall reaction scheme, together with some alternative routes is shown below. The X-ray structures of (4) & (5) are shown in Figures and 4 [3].



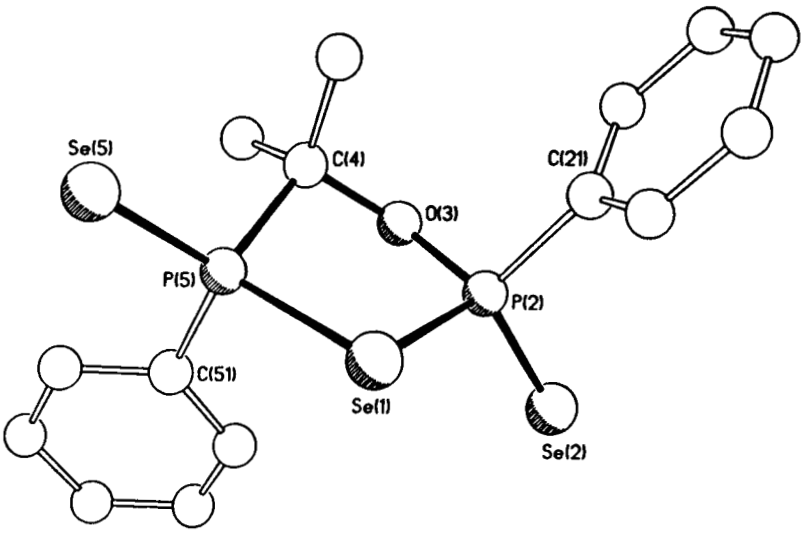


FIGURE 3 The X-ray crystal structure of (4)

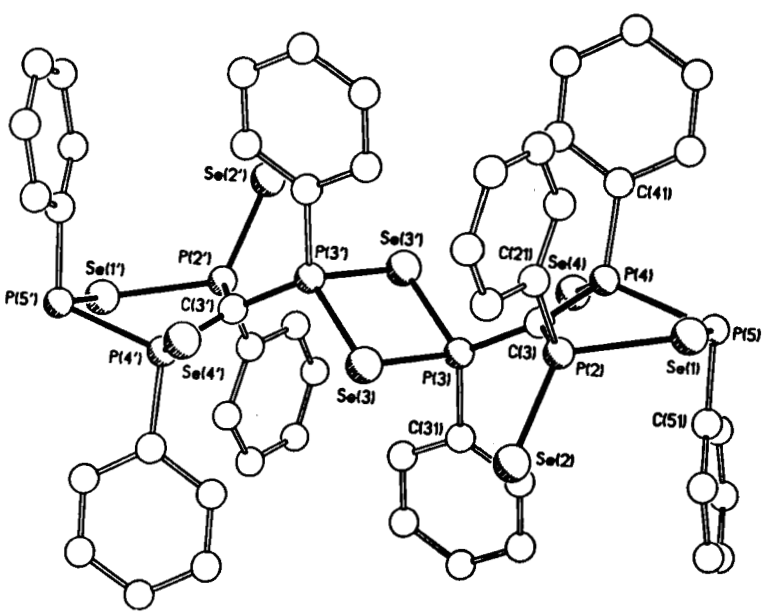


FIGURE 4 The X-ray crystal structure of (5)

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