Preparation of a Symmetrical Tetra-alkyl Monoselenopyrophosphate: Bis-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yl) Selenide

By David S. Rycroft and Raymond F. M. White*

(*Department of Chemistry, Sir John Cass School of Science and Technology, City of London Polytechnic, 31 Jewry Street, London* EC3N 2EY)

Summary Bis-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yl) selenide (I), the first example of a symmetrical tetra-alkyl monoselenopyrophosphate, has been prepared by the reaction of selenous acid with 5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan (II).

In connection with studies of the chemistry of phosphorus esters it is of interest to prepare a symmetrical tetra-alkyl monoselenopyrophosphate.[1] It was reported[1] that methods which had been used successfully to prepare symmetrical tetra-alkyl monothiopyrophosphates had failed to give the selenium analogues, other products being obtained instead. We now describe a novel route to a symmetrical bicyclic tetra-alkyl monoselenopyrophosphate.

Warming of 5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan (II) (2 mol) and selenous acid (1 mol) in benzene–methanol gave an exothermic reaction which had to be cooled in ice to avoid decomposition and formation of red selenium. The crystals obtained were recrystallised from $CHCl_3$–Et_2O. The product, m.p. 164—169°, yield 25%, was shown to be bis-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yl) selenide by elemental analysis (C,H,P,Se) and n.m.r. spectroscopy (^1H, ^{31}P). In particular the symmetrical nature of the pyrophosphate was shown by the ^{31}P n.m.r. spectrum which was obtained using heteronuclear double resonance techniques; the value obtained for the phosphorus chemical shift did not depend on which peak in the ^1H n.m.r. spectrum was monitored. For comparison the asymmetric isomer, *P*-oxo-*P'*-selenobis-(5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl) oxide, was prepared, using a route similar to that for the preparation of the sulphur analogue,[2] from triethylammonium 5,5-dimethyl-2-oxo-2-seleno-1,3,2-dioxaphosphorinan and 5,5-dimethyl-2-chloro-2-oxo-1,3,2-dioxaphosphorinan; the ^1H n.m.r. spectrum showed that the two six-membered rings were different, and the phosphorus nuclei were shown to have different chemical shifts† [$\delta^{31}P(O) = -22{\cdot}9$ p.p.m., $\delta^{31}P(Se) = +43{\cdot}6$ p.p.m., *cf.* $\delta^{31}P = +0{\cdot}6$ p.p.m. for (I)].

The ^1H and ^1H–$\{^{31}P\}$ n.m.r. spectra of the material obtained by concentrating the mother liquor from the reaction mixture showed, in addition to signals from (I), peaks assignable to the secondary phosphoric acid, 5,5-

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† Positive to low field from 85% aqueous phosphoric acid.

dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-ol, presumably resulting from oxidation of the secondary phosphonate (II) by an Se=O group.

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[2] R. S. Edmundson, *J. Chem. Soc.(C)*, 1967, 1635.