A New Synthesis of *P*-Methylphospholes by Flash Vacuum Pyrolysis of the Diphosphines derived from Phosphole Oxide Dimers

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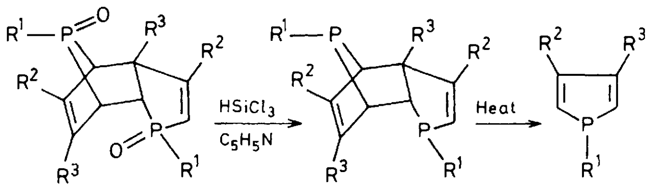
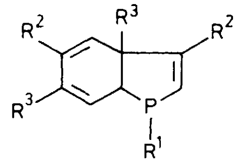
Under thermal conditions where intermolecular interactions are minimized, as in flash vacuum pyrolysis, the diphosphines derived from deoxygenation of *P*-methylphosphole oxide dimers are excellent sources of *P*-methylphospholes.

Phosphole oxide dimers (**1**) are easily deoxygenated with $HSiCl_3$–pyridine to give the corresponding diphosphines[1] (**2**) in yields of about 80%. These compounds have been shown to have some unusual properties associated with the phosphorus atom occupying the highly strained 7-position of a norbornene moiety.[1–3] The diphosphines are formally the dimers of phospholes, but they have never been reported to be formed by thermal treatment of phospholes. We have



(1) (2) (3)

a; R^1 = Me, R^2=R^3=H
b; R^1 = R^2=Me, R^3=H
c; R^1 = R^2 = R^3 = Me



(4)

found, however, that dimers with *P*-methyl substitution can be cleanly converted into the monomeric *P*-methylphospholes if conditions minimizing intermolecular interaction are employed, and this constitutes a useful new synthesis of this type of phosphole. Phospholes are of increasing importance as ligands in co-ordination chemistry; most of this work is being done with the readily accessible[4] *P*-phenyl derivatives, however, and little is known about the *P*-methyl series.

The preferred conditions for the de-dimerization employ the short contact at high temperature provided by the flash vacuum pyrolysis[5] (F.V.P.) technique. The dimers (**2**) were vapourized from a distillation bulb in a Kugelrohr oven into a heated 35 × 1.5 (i.d.) cm evacuated tube packed with glass helices (1.5 mm). The tube was kept at 400 °C (external thermocouple), and the pressure was maintained at 0.25 mmHg for (**2a**) and (**2b**), and at 0.6 mmHg for the more stable (**2c**). Gases were allowed to impinge on a surface chilled by a solid CO_2–acetone bath. ^{31}P N.m.r. analysis of the collected product showed in every case that the product was the corresponding phosphole. None of the starting diphosphine survived the process; the only contaminant (about 5—10%) was the dihydrophosphindole (**4**), some or all of which had been introduced as a contaminant in the diphosphine. Simple distillation, however, allowed easy separation of the more volatile phospholes, which were then pure as shown by the n.m.r. spectroscopic methods used. Yields from the diphosphines were: (**3a**) 97, (**3b**) 91, and (**3c**) 94%. Each product, was fully characterized by ^1H, ^{31}P, and ^{13}C n.m.r. spectroscopy, and the data matched those reported previously [(**3a**),[6,7] (**3b**),[7,8] (**3c**)[7,8]].

Overall yields of the phospholes from the starting 3-phospholene oxides (employing bromine addition and dehydrobromination with triethylamine to generate the dimer oxides[9]) were (**3a**) 38, (**3b**) 50, and (**3c**) 44%. The synthesis of 1-methylphosphole is far superior to the only other known method[6] (9% overall yield from 1-methyl-3-phospholene oxide on bromination, deoxygenation, dehydrohalogenation), which gave a product of only 85% purity. Phospholes (**3b**) and (**3c**) have been more readily prepared[8] by the dehydrohalogenation of the diene–phosphonous dichloride adducts (12 and 13%, respectively).

The isomer[2] of (**2b**) with R^1 of the P-bridge *anti* also gave 1,3-dimethylphosphole (91%) under the same F.V.P. conditions used for (**2b**). Diphosphines with *P*-phenyl substituents, however, did not provide phospholes; these compounds require a higher temperature for volatilization and decompose to dihydrophosphindoles in this step.

Thermal treatment of the dimers in inert solvents is not useful for phosphole synthesis. In solutions of concentration greater than about 0.5—1.0 M, little phosphole is formed and intermolecular interactions lead to quite complex mixtures. In more dilute solutions, phosphole formation does occur as the major pathway, but the dimers are slow to react; only about half of dimer (**2**) in a 0.05 M n-decane solution was decomposed after 17 h at 120 °C. These studies will be described elsewhere.

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