

## Synthesis of the First Examples of 1-Benzophosphepines

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Flash vacuum pyrolysis of 2a,7b-dihydro-3-phenyl-3*H*-cyclobut[*b*]phosphindole 3-oxide **4**, prepared from 1-phenyl-1*H*-phosphindole 1-oxide **1** via three steps, results in ring-opening to give 1-phenyl-1-benzophosphepine 1-oxide **5**, which, on treatment with trichlorosilane, undergoes deoxygenation to afford 1-phenyl-1-benzophosphepine **6**.

A variety of fully unsaturated seven-membered heterocyclic rings (heteroepines) containing nitrogen such as azepines,<sup>1a</sup> diazepines,<sup>1b,2</sup> triazepines<sup>3</sup> and oxazepines<sup>4</sup> have been prepared as relatively stable compounds. However, heteroepines containing phosphorus, which belongs to the same group as nitrogen in the periodic table of elements are known to be thermolabile, in analogy with thiepinines,<sup>5,6</sup> and only two examples of phosphepines have been reported.<sup>7,8</sup> 2,7-Di-*tert*-butyl-1-phenylphosphepine is prepared from 4,4-dimethylpent-2-ynal via two steps<sup>7</sup> and 3-phenyl-3-benzophosphepine is obtained by the reaction of *o*-diethynylbenzene with phenylphosphine.<sup>8</sup> We report here the synthesis of the first examples of 1-benzophosphepines.

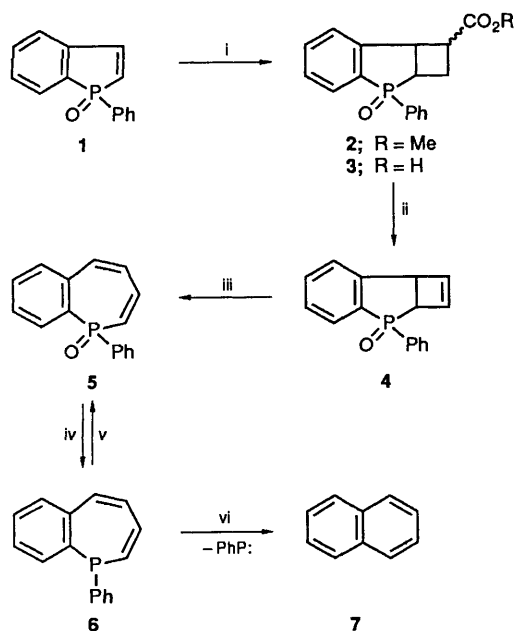
The phosphindole **1**<sup>9</sup> was irradiated with methyl acrylate to give the adduct **2**,<sup>†</sup> which was hydrolysed and then oxidatively decarboxylated by treatment with lead tetraacetate giving the starting dihydrocyclobut[*b*]phosphindole **4** via the acid **3** in *ca.* 30% yield from **1**. Although the tricyclic compound **4** was

heated in solvents at 190 °C, no reaction occurred. However, flash vacuum pyrolysis (550 °C) of **4** resulted in valence isomerization with ring-opening to give the desired 1-phenyl-1-benzophosphepine 1-oxide **5** (m.p. 128–130 °C) in 85% yield,<sup>‡</sup> along with naphthalene (2–5%). In view of the high temperature required for this reaction, the ring conversion of **4** into **5** may proceed via homolytic cleavage of the cyclobutene ring, by analogy with the related thermal ring-opening of bicycloheptenes<sup>10</sup> and tricyclooctanes.<sup>11</sup>

The deoxygenation of **5** was achieved by treatment with trichlorosilane followed by hydrolysis to afford 1-phenyl-1-

<sup>‡</sup> Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds reported. *Selected data:* **5** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 6.40 (1 H, dd, 2-H), 6.45 (1 H, ddd, 4-H), 6.98 (1 H, ddd, 3-H), 7.08 (1 H, d, 5-H) and 7.3–8.1 (9 H, m, Ph-H), *J*<sub>P,2</sub> 12.0, *J*<sub>P,3</sub> 41.0, *J*<sub>P,4</sub> 1.7, *J*<sub>2,3</sub> 12.9, *J*<sub>3,4</sub> 6.4 and *J*<sub>4,5</sub> 12.7 Hz; <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 124.6 (*J*<sub>P,C</sub> 98 Hz, C-2), 127.6 (C-4), 136.6 (C-5) and 138.6 (C-3); **6** <sup>1</sup>H NMR δ 6.06 (1 H, d, 2-H), 6.51 (1 H, ddd, 3-H), 6.55 (1 H, dd, 4-H), 7.15 (1 H, d, 5-H) and 7.1–7.8 (9 H, m, Ph-H), *J*<sub>P,2</sub> 11.3, *J*<sub>P,3</sub> 20.5, *J*<sub>2,3</sub> 11.3, *J*<sub>3,4</sub> 5.5 and *J*<sub>4,5</sub> 12.1 Hz; <sup>13</sup>C NMR δ 131.2 (*J*<sub>P,C</sub> 8 Hz, C-4), 133.6 (*J*<sub>P,C</sub> 16 Hz C-2), 135.6 (*J*<sub>P,C</sub> 21 Hz, C-3) and 136.3 (*J*<sub>P,C</sub> 8 Hz, C-5).

<sup>†</sup> Compound **2** was obtained as a 3:2 mixture of two stereoisomers, but used in the following reactions without separation.



**Scheme 1** Reagents and conditions: i, methyl acrylate, benzene, irradiation (400 W, high-pressure Hg lamp), 3–4 h, 65%; ii,  $Pb(OAc)_4$ ,  $Cu(OAc)_2$ , pyridine, benzene, 90–95 °C, 1.5 h, 55%; iii, flash vacuum pyrolysis ( $6.0 \times 10^{-5}$  mmHg, 550 °C), 85%; iv,  $SiHCl_3$ , benzene, 55 °C, 5 h; NaOH,  $H_2O$ , 80%; v, *m*-chloroperbenzoic acid,  $CH_2Cl_2$ , 0 °C, 30 min, quant.; vi, heat (60–80 °C), benzene or toluene, 95%

benzophosphine **6** (m.p. 84–85 °C) in 80% yield.‡ The phosphapine **6** reverted quantitatively to the oxide **5** on oxidation with *m*-chloroperbenzoic acid.

The phosphapine oxide **5** is thermally stable and remained largely unchanged even when heated in xylene at 180 °C for 24 h. However, the deoxygenated phosphapine **6** is thermolabile in solution and gradually decomposes to naphthalene, probably *via* a norcaradiene intermediate, by analogy with borepines<sup>12</sup> and thiepinis,<sup>6</sup> whereas in a dry solid state it can

be kept for several weeks at room temperature without decomposition. The half-life of **6** estimated by the NMR spectroscopic analysis in toluene at 80 °C is about 90 min. This thermal behaviour is similar to that of 3-phenyl-3-benzophosphine<sup>8</sup> (half-life in decalin at 80 °C: 120 min), whose 3-oxide is also thermally stable.

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