Alkylation of 2-bromophosphinines using lithium trialkylborohydrides

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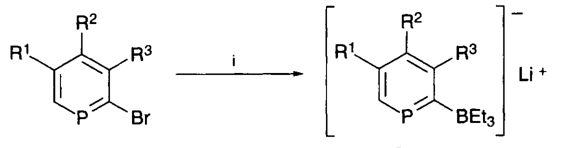
2-Bromophosphinines are converted into 2-ethylphosphinines by successive reactions with lithium triethylborohydride and iodine.

Hydroboration reactions of phosphaalkenes have already been the subject of several theoretical[1] and practical studies.[2,3] They produce either P–B or C–B bonds, depending upon the polarity of the P=C bond. *A priori,* phosphinines should undergo hydroboration to give C–B bonds because their phosphorus atoms bear a substantial positive charge.[4] Thus, in the course of a systematic investigation of the various possible ways to functionalize phosphinines, we studied their reactions towards boron hydride reagents. We report here our preliminary results.

The reaction of two equivalents of lithium triethylborohydride with 2-bromophosphinines[5,6] in THF at room temperature cleanly gives the corresponding borates. (Scheme 1).

Monitoring the reaction by ^{31}P NMR spectroscopy shows that the conversion of **1** into **2**† is almost quantitative. The ^{31}P resonance is shifted to low field by *ca.* 20 ppm upon boration of each phosphinine. The most obvious change in the ^{1}H spectra after boration is the dramatic increase of the $^{3}J_{H-P}$ coupling within the ring, *e.g.* $^{3}J_{H-P}$ = 4.3 Hz for **1c** and $^{3}J_{H-P}$ = 16.2 Hz for **2c**. A similar increase of the $^{3}J_{H-P}$ coupling constant has been observed upon insertion of zirconocene into the C–Br bond of **1c**.[7] The first step of the transformation very probably involves a hydroboration of the formal P=C(Br) double bond to create a P–H and a C–B bond; this is followed by a rearomatisation of the ring by elimination of HBr, wherein the second borohydride molecule acts as a base.

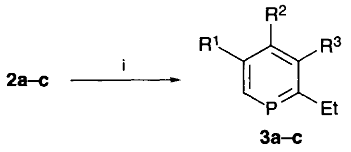
One straightforward application of these phosphinine-borates is their transformation into the corresponding 2-ethylphosphinines by reaction with iodine, according to the classical scheme (Scheme 2).[8],†



1a–c **2a–c**

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

Scheme 1 *Reagents and conditions:* i, LiBEt$_3$H (2 equiv.), THF, 25 °C, 1 h



3a–c

Scheme 2 *Reagents and conditions*: i, I$_2$ (1.1 equiv.), THF, 25 °C, 10 min

This conversion represents the only practical method for the alkylation of phosphinines known to date. The two transformations (**1** → **2** → **3**) can be carried out in one pot and the overall yields, isolated by chromatography, are high *ca.* 70%. We are currently exploring other applications of these phosphinine-borates.

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Footnote

† *Selected data* for **2a**: ^{31}P NMR (81.01 MHz, THF) δ 229.40. For **2b**: ^{31}P (THF) δ 237.5 For **2c**: ^{31}P (THF) δ 214.7; ^{1}H NMR (200.13 MHz, C_6D_6) δ 0.75–1.40 (m, 15 H, Et), 2.30 (m, 6 H, Me), 8.38 (d, $^{2}J_{HP}$ 31.10, 6-H), 8.40 (d, $^{3}J_{HP}$ 16.20, 3-H); ^{13}C NMR (50.32 MHz), C_6D_6) δ 12.20 (s, Me), 18.30 (q, J_{CB} 40.80, CH$_2$–B), 23.10 (s, Me), 23.55 (s, Me), 134.10 (d, J_{CP} 23.60, C-5 or C-4), 140.40 (d, $^{2}J_{CP}$ 14.20, C-3) and 153.20 (d, $^{1}J_{CP}$ 49.30, C-6). For **3a**: ^{31}P NMR (THF) δ 203.0; ^{1}H NMR (CDCl$_3$) δ 1.37 (t, 3 H, $^{3}J_{HH}$ 7.60, Me), 3.01 (p, 2 H, $^{3}J_{HP}$ = $^{3}J_{HH}$ 7.30, CH$_2$), 7.50 (qq, 1 H, $^{3}J_{HH}$ 8.80, $^{3}J_{HH}$ 7.90, $^{4}J_{HH}$ 0.45, $^{4}J_{HP}$ 4.0, 4-H), 7.72 (m, 1 H, $^{3}J_{HH}$ 8.80, $^{4}J_{HH}$ 0.45, $^{3}J_{HP}$ not measured, 3-H), 7.75 (m, 1 H, $^{3}J_{HP}$ 10.20, $^{3}J_{HH}$ 7.90, $^{4}J_{HH}$ 0.45, $^{3}J_{HP}$ not measured, 5-H) and 8.73 (ddd, 1 H, $^{2}J_{HP}$ 37.50, $^{3}J_{HH}$ 10.20, $^{4}J_{HH}$ 0.45, 6-H); ^{13}C NMR (CDCl$_3$) δ 18.30 (d, $^{3}J_{CP}$ 9.30, Me), 32.60 (d, $^{2}J_{CP}$ 32.20, CH$_2$), 129.45 (d, $^{2}J_{CP}$ 18.40, C-3), 131.60 (d, $^{3}J_{CP}$ 14.30, C-4), 133.70 (d, $^{2}J_{CP}$ 12.60, C-5), 154.60 (d, $^{1}J_{CP}$ 52.60, C-6), 175.60 (d, $^{1}J_{CP}$ 52.50, C-2). For **3b**: ^{31}P (CDCl$_3$) δ 206.30; ^{1}H NMR (CDCl$_3$) δ 1.30 (t, 3 H, $^{3}J_{HH}$ 7.50, Me), 2.45 (d, 3 H, $^{4}J_{HP}$ 2.0, Me), 3.0 (p, 2 H, $^{3}J_{HH}$ = $^{3}J_{HP}$ 7.50, CH$_2$), 7.33 (dd, 1 H, $^{3}J_{HH}$ 8.20, $^{4}J_{HP}$ 4.60, 4-H), 7.63 (dt, 1 H, $^{3}J_{HH}$ = $^{3}J_{HP}$ 10.0, $^{3}J_{HH}$ 8.20, 5-H) and 8.55 (dd, 1 H, $^{2}J_{HP}$ 38.0, $^{3}J_{HH}$ 10.0, 6-H); ^{13}C NMR (CDCl$_3$) δ 17.40 (d, $^{3}J_{CP}$ 8.0, Me), 21.85 (s, Me), 30.35 (d, $^{2}J_{CP}$ 35.20, CH$_2$), 132.70 (d, J_{CP} 14.60, C-5 or C-4), 133.20 (d, J_{CP} 18.10, C-4 or C-5), 142.40 (d, $^{2}J_{CP}$ 12.20 C-3), 153.10 (d, $^{1}J_{CP}$ 49.80, C-6) and 172.40 (d, $^{1}J_{CP}$ 51.60, C-2). For **3c**: ^{31}P (CDCl$_3$) δ 184.40; ^{1}H NMR (CDCl$_3$) δ 1.35 (t, 3 H, $^{3}J_{HH}$ 7.50, Me), 2.40 (d, 3 H, J_{HP} 3.30, Me), 2.43 (s, 3 H, Me), 2.95 (p, 2 H, $^{3}J_{HH}$ = $^{3}J_{HP}$ 7.50, CH$_2$), 7.60 (d, 1 H, $^{3}J_{HP}$ 6.67, 3-H) and 8.43 (d, 1 H, $^{2}J_{HP}$ 37.45, 6-H); ^{13}C NMR (CDCl$_3$) δ 19.0 (d, $^{3}J_{CP}$ 9.70, Me), 23.10 (s, Me), 23.60 (s, Me), 32.80 (d, $^{2}J_{CP}$ 32.0, CH$_2$), 137.20 (d, $^{2}J_{CP}$ 12.70, C-3), 139.70 (d, J_{CP} 17.10, C-4 or C-5), 141.60 (d, J_{CP} 49.60, C-6) and 173.80 (d, $^{1}J_{CP}$ 48.40, C-2).

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