Platinum catalysed 1,4-diboration of α,β-unsaturated ketones

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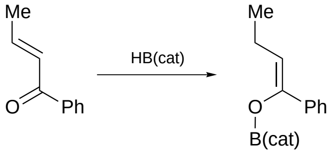
Diborane(4) compounds react with α,β-unsaturated ketones to give the 1,4-addition product in the presence of a platinum catalyst at 80 °C.

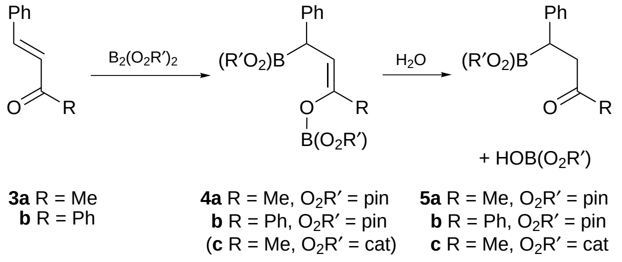
In contrast with the rhodium-catalysed hydroboration of alkenes, alkynes and α,β-unsaturated carbonyl compounds, which is now well established,[1] the related topic of metal-catalysed diboration reactions has only recently been studied in any detail. Thus the groups of Baker and Marder,[2] Miyaura[3] and Smith[4] have shown that alkenes can be diborated in the presence of rhodium,[2] gold[2] or platinum[3,4] catalysts affording 1,2-bis(boronate) ester products, whilst platinum catalysed alkyne diboration yielding *cis*-1,2-bis(boronate) alkenes has been demonstrated by Miyaura and coworkers,[5a,b] Iverson and Smith[5c,d] and Norman and coworkers.[5e] Additional studies by Miyaura and coworkers[6] have also demonstrated 1,4-addition of a B–B bond to 1,3-dienes. In all cases, key steps are thought to involve oxidative addition of the B–B bond of a diborane(4) compound to the metal centre followed by coordination and insertion of the organic precursor and subsequent reductive elimination of the product.[7]

To date, however, the reaction of α,β-unsaturated carbonyl compounds with diborane(4) compounds has not been studied, although previous work has shown that HB(cat) (cat = 1,2-$O_2C_6H_4$) reacts with α,β-unsaturated carbonyl compounds in a 1,4 fashion[8] to give a synthetically useful[9] boron enolate as shown in Scheme 1. Here we report the reaction of α,β-unsaturated ketones with the diborane(4) compounds $B_2(pin)_2$ **1**[10] (pin = $OCMe_2CMe_2O$) and $B_2(cat)_2$ **2**.[11]



Scheme 1

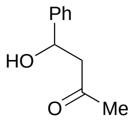
Reaction of *trans*-4-phenylbut-3-en-2-one **3a** or *trans*-1,2-diphenylprop-2-en-1-one **3b** with 1 equiv. of **1** in the presence of 5 mol% of $[Pt(C_2H_4)(PPh_3)_2]$ at 80 °C gave, after 12 h, the 1,4-bis(boronate) ester products **4a**,**b** quantitatively as judged by ^1H NMR spectroscopy (Scheme 2).‡ Furthermore, the ^1H NMR spectra of **4a** and **4b** showed that each was present as only a single isomer which, in the case of **4a** and, by implication **4b**, is assumed to be the *Z*-isomer on the basis of a ^1H NMR NOE signal enhancement (13.1%) between the vinylic and methyl protons; both hydroboration of α,β-unsaturated ketones[8] and diboration of dienes[5] also produce only the *Z*-isomer. Compounds **4a** and **4b** are both sensitive to hydrolysis and exposure to H_2O affords the hydrolysis products **5a** and **5b** (Scheme 2).§



Scheme 2

In the corresponding reaction between **3a** and **2**, the 1,4-bis(boronate) ester **4c** analogous to **4a**,**b** was not observed but the hydrolysis product, **5c**, was identified by ^1H NMR spectroscopy.¶ This observation indicates that the initial products formed from reactions involving **2** are more susceptible to hydrolysis than those involving **1** in keeping with observations made in the diboration of alkynes.[5e]

As further confirmation of the nature of the products formed in these reactions, compounds **5a** and **5c** were oxidised using NaOH–H_2O_2 to give the corresponding alcohol **6**‖ which was identified by the comparison of the spectra obtained with lit. values.[12]



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Comparison of **4a**,**b** with the products formed from the hydroboration of similar α,β-unsaturated ketones shows that the regiochemistry is similar in both reactions, *i.e.* 1,4-addition occurs. However the reaction of diborane(4) compounds with α,β-unsaturated ketones results in the effective formation of a hydroxyl group in the β position (*i.e.* compound **6** in the case of **4a**), in contrast to hydroboration where no hydroxyl group is formed but in which the alkene function is effectively reduced.

We note finally that boron enolates such as **4a**,**c** are likely to be useful intermediates in organic synthesis providing starting materials in processes such as aldol condensations with aldehydes.[9] Reactions, of α,β-unsaturated ketones with chiral diborane(4) compounds will be reported elsewhere.

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Footnotes and References

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‡ *Synthesis* of **4a**: to a Schlenk tube charged with **1** (0.020 g, 0.079 mmol), $[Pt(C_2H_4)(PPh_3)_2]$ (5 mol%) and **3a** (0.013 g, 0.087 mmol), toluene (5 cm^3) was added and the reaction heated at 80 °C for 12 h. After this time the toluene was removed by vacuum affording a red oil containing **4a** as the major product (0.030 g, 90%) (the red colour is due to traces of decomposed catalyst). Compound **4b** was prepared similarly. *NMR data*: **4a**: ^1H (300 MHz, C_6D_6) δ 7.6–7.1 (m, 5 H, Ph), 5.40 (dq, 1 H, C=CH, $^3J_{HH}$ 8.7, $^4J_{HH}$ 1.0 Hz), 4.06 [br d, 1 H, C*H*(B)Ph, $^3J_{HH}$ 8.7 Hz, coupling to Me not resolved

owing to broadening resulting from the adjacent boron], 2.05 (dd, 3 H, Me, $^4J_{\mathrm{HH}}$ 1.0, $^5J_{\mathrm{HH}}$ 1.0 Hz), 1.06 [s, 6 H, B(OC*Me*$_2$CMe$_2$O)], 1.04 [s, 6 H, B(OCMe$_2$C*Me*$_2$O)], 1.03 [s, 12 H, OB(OC*Me*$_2$C*Me*$_2$O)]; ^{13}C{^{1}H} (75.4 MHz, C_6D_6) δ 146.5 (*ipso*-Ph), 143.6 [=*C*(Me)], 129.5, 129.1, 128.9 (Ph), 112.0 (=CH), 83.5, 83.0 [B(O*C*Me$_2$*C*Me$_2$O)], 25.3, 24.9, 24.7 [B(OC*Me*$_2$C*Me*$_2$O)], 21.6 (Me), *C*H(B)Ph not observed; ^{11}B{^{1}H} (96.3 MHz, C_6D_6) δ 30.8 (1B, CB), 20.0 (1B, OB). **4b**: ^{1}H (300 MHz, C_6D_6) δ 7.3–7.0 (m, 10 H, Ph), 5.82 (d, 1 H, C=CH, $^3J_{\mathrm{HH}}$ 8.7 Hz), 3.54 [br d, 1 H, C*H*(B)Ph, $^3J_{\mathrm{HH}}$ 8.7 Hz], 1.16 [s, 6 H, B(OC*Me*$_2$CMe$_2$O)]; 1.14 [s, 6 H, B(OCMe$_2$C*Me*$_2$O)], 1.12 [s, 12 H, OB(OC*Me*$_2$CMe$_2$O)]; ^{13}C{^{1}H} (75.4 MHz, C_6D_6) δ 146.9 [=*C*(Ph)], 141.9, 141.7 (*ipso*-Ph), 128.3, 128.2, 128.1, 128.0, 125.3, 124.4 (Ph), 112.8 (=CH), 83.5, 83.3 [B(O*C*Me$_2$*C*Me$_2$O)], 30.0 [br, *C*H(B)Ph], 24.7, 24.6, 23.0 [B(OC*Me*$_2$C*Me*$_2$O)]; ^{11}B{^{1}H} (96.3 MHz, C_6D_6) δ 30.6 (1B, CB), 19.5 (1B, OB).

§ *Synthesis* of **5a**; Hydrolysis of **4a** was achieved by addition of H_2O (0.5 cm^3) to a solution of **4a** (0.20 g, 0.5 mmol) in toluene (2 cm^3), removal of both the solvents by vacuum and extraction of the residue into hexane (3 × 1 cm^3) affording **5a** as a colourless oil (0.137 g, 100%). Compound **5b** was prepared similarly. *NMR data*: **5a**: ^{1}H (400 MHz, $CDCl_3$) δ 7.25 (m, 5 H, Ph), 3.04 [dd, 1 H, C*H*(B)Ph/C*H*$_2$, $^3J_{\mathrm{HH}}$ 11.0, $^3J_{\mathrm{HH}}$ 18.3 Hz], 2.83 [dd, 1 H, C*H*(B)Ph/C*H*$_2$, $^3J_{\mathrm{HH}}$ 5.1, $^3J_{\mathrm{HH}}$ 18.3 Hz], 2.64 [dd, 1 H, C*H*(B)Ph/C*H*$_2$, $^3J_{\mathrm{HH}}$ 5.1, $^3J_{\mathrm{HH}}$ 11.0 Hz], 2.14 (s, 3 H, Me), 1.22 [s, 6 H, B(OC*Me*$_2$CMe$_2$O)], 1.16 [s, 6 H, B(OCMe$_2$C*Me*$_2$O)]; ^{13}C{^{1}H} (75.4 MHz, C_6D_6) δ 206.6 (CO), 142.7 (*ipso*-Ph), 128.7, 128.6, 125.7 (Ph), 83.3 [B(O*C*Me$_2$*C*Me$_2$O)], 47.5 (*C*H$_2$), 28.9 (Me), 24.7 [B(OC*Me*$_2$CMe$_2$O)], 24.6 [B(OCMe$_2$C*Me*$_2$O)], *C*H(B)Ph not observed; ^{11}B{^{1}H} (96.3 MHz, C_6D_6) δ 31.3. **5b**: ^{1}H (300 MHz, $CDCl_3$) δ 8.00–7.00 (m, 10 H, Ph), 3.49 [dd, 1 H, C*H*(B)Ph/C*H*$_2$, $^3J_{\mathrm{HH}}$ 10.8, $^3J_{\mathrm{HH}}$ 18.3 Hz], 3.35 [dd, 1 H, C*H*(B)Ph/C*H*$_2$, $^3J_{\mathrm{HH}}$ 5.1, $^3J_{\mathrm{HH}}$ 18.3 Hz], 2.72 [dd, 1 H, C*H*(B)Ph/C*H*$_2$, $^3J_{\mathrm{HH}}$ 5.1, $^3J_{\mathrm{HH}}$ 10.8 Hz], 1.17 [s, 6 H, B(OC*Me*$_2$CMe$_2$O)], 1.10 [s, 6 H, B(OCMe$_2$C*Me*$_2$O)]; ^{13}C{^{1}H} (75.4 MHz, C_6D_6) δ 199.7 (CO), 144.9, 142.0 (*ipso*-Ph), 132.9, 129.0, 128.5, 128.4, 128.0, 125.6 (Ph), 83.4 [B(O*C*Me$_2$*C*Me$_2$O)], 43.3 (CH_2), 24.6 [B(OC*Me*$_2$CMe$_2$O)], 24.5 [B(OCMe$_2$C*Me*$_2$O)], *C*H(B)Ph not observed; ^{11}B{^{1}H} (96.3 MHz, $CDCl_3$) δ 30.8.

¶ *NMR data* for **5c**: ^{1}H (300 MHz, C_6D_6) δ 6.75 (m, 5 H, Ph), 6.45 [m, 4 H, B(1,2-$O_2C_6H_4$)], 2.64 [dd, 1 H, C*H*(B)Ph/C*H*$_2$, $^3J_{\mathrm{HH}}$ 6.1, $^3J_{\mathrm{HH}}$ 9.2 Hz], 2.48 [dd, 1 H, C*H*(B)Ph/C*H*$_2$, $^3J_{\mathrm{HH}}$ 9.2, $^3J_{\mathrm{HH}}$ 18.6 Hz], 2.24 [dd, 1 H, C*H*(B)Ph/C*H*$_2$, $^3J_{\mathrm{HH}}$ 6.1, $^3J_{\mathrm{HH}}$ 18.6 Hz], 1.61 (s, 3 H, Me); ^{13}C{^{1}H} (75.4 MHz, C_6D_6) δ 210.0 (CO), 149.4 [C^{1,2} of B(1,2-$O_2C_6H_4$)], 142.9 (*ipso*-Ph), 128.7, 128.6, 125.9 (Ph), 122.5 [C^{4,5} of B(1,2-$O_2C_6H_4$)], 112.6 [C^{3,6} of B(1,2-$O_2C_6H_4$)], 48.5 (CH_2), 28.1 (Me), *C*H(B)Ph not observed; ^{11}B{^{1}H} (96.3 MHz, C_6D_6) δ 32.5.

‖ *Synthesis* of **6**: To a solution of **4a** (0.050 g, 0.18 mmol) in thf (1 cm^3), samples of EtOH (1 cm^3), NaOH(aq) (1 cm^3 of a 1 M solution) and H_2O_2 (30 vol%, 1 cm^3) (CAUTION: peroxides and organic solvents can be explosive) were added and the reaction mixture stirred at room temp. for 12 h. After this time the crude product was extracted into Et_2O (2 × 5 cm^3), dried ($MgSO_4$) and evaporated to dryness affording **6** as an oily solid (0.024 g, 80%).

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