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Microwave mediated rhodium-catalysed hydroboration of *trans*-4-octene with pinacolborane

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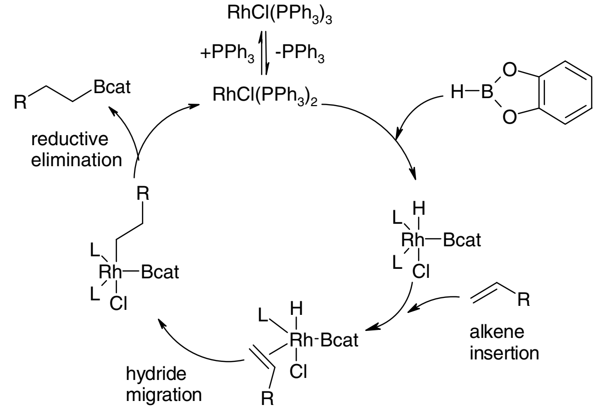
Abstract—Hydroboration of *trans*-4-octene by pinacolborane was carried out using oxidised Wilkinson's catalyst to afford 1-octanol in high yields. Wilkinson's catalyst in conjunction with microwave irradiation also provided a convenient and rapid route to the terminal pinacolboronate ester.

The importance of alkane and alkene boronic esters as useful intermediates in organic synthesis, has attracted much attention in hydroboration reactions[1] utilising catecholborane as the hydroborating agent. Alkane and alkene boronic esters are easily produced from catecholborane at elevated reaction temperatures (such as 70 °C for alkynes and 100 °C for alkenes).[2] These esters can easily be converted to the corresponding boronic acids by subsequent hydrolysis.[3]

Due to the fact that elevated temperatures are required in order to access the boronic esters, a number of research groups have focused their attention on catalytic hydroboration with early transition metal complexes, in order to develop new, convenient, and cost-effective catalytic routes for hydroboration.[4,5] Titanium complexes such as Cp_2TiCl_2,[6] $TiCl_3$,[7] and $Ti(O\text{-}Pr^i)_4$[8] have been reported to enhance the rate of hydroboration. However, some research groups have shown that these reactions are, in fact, not catalysed by the transition metal species but rather assist in the rapid degradation of catecholborane to afford diborane, which in turn, effects subsequent hydroboration.[9,10] Männig and Nöth[11] reported the first example of rhodium-catalysed hydroboration of alkenes in 1985 (Scheme 1). This catalyst ($RhCl(PPh_3)_3$, Wilkinson's catalyst) was different from the transition metals mentioned above, and demonstrated a less pronounced decomposition of catecholborane.



Scheme 1. Mechanism of $RhCl(PPh_3)_3$-catalysed hydroboration, by Männig and Nöth.[11]

Subsequently, Evans et al.[12] screened a number of other transition metal complexes for catalytic activity in the hydroboration of 1-decene with catecholborane. Their study concluded that rhodium complexes are the most suitable catalysts for hydroboration. Recently, Evans et al.[13] also conducted deuterium labelling studies in order to provide additional information on the mechanism for the Rh(I)-catalysed hydroboration initially described by Männig and Nöth.[11]

The results of the deuterium labelling studies clearly showed that deuterium was not only incorporated at the α- and β-carbons of the product alcohol as expected, but was also found in the recovered olefins from the

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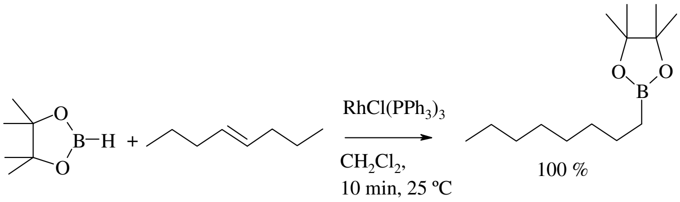


Scheme 2. Hydroboration of *trans*-4-octene with pinacolborane catalysed by $RhCl(PPh_3)_3$.[15,16]

reaction of 1-decene with deuteriocatecholborane catalysed by $Rh(PPh_3)_3Cl$. This interesting observation demonstrated that the mechanism of catalysed hydroboration was not as simple as presented initially by Männig and Nöth. In this investigation, Evans et al.[13] proposed a mechanism that showed no less than six deuterium containing compounds that are expected to form if the olefin complexation to rhodium and hydride migration are in fact reversible.[13] This study also revealed that the route followed by Rh(I)-catalysed hydroboration is substrate dependent. For 1-decene, the reductive elimination was found to be the regioselectivity-determining step, while the hydride migration determines the regioselectivity for styrene.[13]

In the early 1990s, Tucker et al. reported a new hydroborating agent, pinacolborane, which, when compared to catecholborane afforded a greater level of regio- and stereoselectivity.[14] It has also been reported that the hydroboration of alkenes with pinacolborane is not catalysed by Wilkinson's catalyst $RhCl(PPh_3)_3$.[14] In this paper, we report the successful $RhCl(PPh_3)_3$-catalysed hydroboration and isomerisation route with *trans*-4-octene and pinacolborane assisted by microwave irradiation.

Pereira and Srebnik[15,16] reported that as little as 0.2 mol % of $RhCl(PPh_3)_3$, catalyses hydroboration of *trans*-4-octene effectively to afford exclusively, the terminal octyl-pinacolboronate ester (Scheme 2). The results prompted our own investigation into this reaction.

We repeated this reaction several times, monitoring the reaction progress with ^{11}B NMR spectroscopy. However, to our surprise, no formation of pinacolboronates was detected after 24 h at ambient temperature. This was in stark contrast to the reported catalytic activity (!).[15,16] Our own observations were supported by Tucker et al.,[14] whose earlier attempts at the same reaction were also unsuccessful. Failure to hydroborate *trans*-4-octene with pinacolborane under catalytic conditions was attributed to the sterically demanding nature of *trans*-4-octene, when compared to the successful hydroboration of 1-octene under the same conditions. In 2004, Yamamoto et al.[17] also failed to reproduce results reported by Pereira and Srebnik.[15,16]

It has been reported that Wilkinson's catalyst can be activated for hydrogenation, by treatment with oxygen or hydrogen peroxide.[18] In the early 1970s, Barnett et al.[19] employed O_2-treated $RhCl(PPh_3)_3$ to accelerate the rate of ring opening of bicycloalkenes, and this showed that molecular oxygen does play a role in activating the Wilkinson's catalyst. Bennett and Donaldson[20] reported a crystal structure (Fig. 1) obtained from concentrated, oxygen-saturated solutions of $RhCl(PPh_3)_3$, which may correspond to the activated catalyst.

We subsequently employed O_2-treated $RhCl(PPh_3)_3$ in order to investigate, using ^{11}B NMR spectroscopy, the effect of molecular oxygen on the reaction of pinacolborane with *trans*-4-octene. Our results showed a dramatic increase in catalytic activity. ^{11}B NMR spectroscopy detected 72% of the octyl-pinacolboronate ester after 48 h at 25 °C. After oxidative work-up of the product mixture followed by ether extractions, GC analysis of the product showed 100% 1-octanol. The enhanced activity may be attributed to the fact that the metal centre of the oxidised catalyst is more electrophilic than that of $RhCl(PPh_3)_3$. The geometry of the rhodium atom has also been reported to change upon coordination of molecular oxygen, from planar to trigonal bipyramidal.[20]

During the course of optimising our reactions, we also investigated the use of microwave irradiation in the rhodium-catalysed hydroboration reactions of *trans*-4-octene with pinacolborane. To our delight, the ^{11}B NMR spectroscopic results showed 73% of the octyl-pinacolboronate ester after irradiating a mixture of *trans*-4-octene, Wilkinson's catalyst, and pinacolborane in an NMR tube with 100 W of microwave energy for 20 min with concomitant cooling (reaction temperature maintained at 25 °C; Scheme 3; Figs. 2 and 3),[21] in dry THF.[22] The formation of octyl-pinacolboronate was confirmed by GC/MS, which gave a molecular ion of *m*/*z* 241 attributed to octyl-pinacolboronate ester (MW = 240.2 g/mol).

According to the above data, it can be concluded that freshly prepared $RhCl(PPh_3)_3$ fails to catalyse hydroboration of *trans*-4-octene with pinacolborane,[17] whereas O_2-treated $RhCl(PPh_3)_3$ shows enhanced catalytic activity in hydroboration reactions, and in conjunction with microwave irradiation, provides an effective and conve-

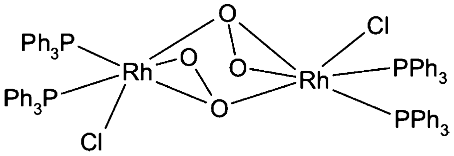
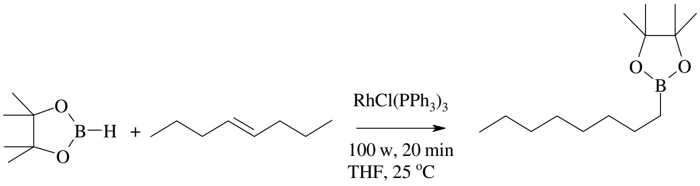


Figure 1. Crystal structure obtained by Bennett and Donaldson from oxygen-treated $RhCl(PPh_3)_3$.[20]



Scheme 3. Microwave-assisted RhC(PPh$_3$)$_3$-catalysed hydroboration of *trans*-4-octene with pinacolborane.

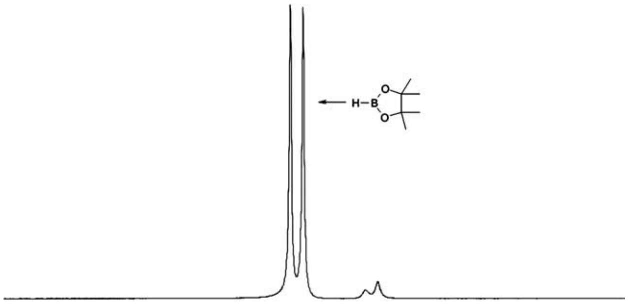


Figure 2. ^{11}B NMR spectrum of pinacolborane in THF.

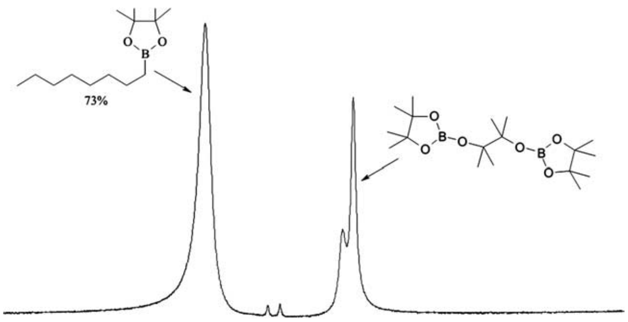


Figure 3. ^{11}B NMR spectrum of 2-octyl-pinacolboronate ester in THF.

nient route for hydroboration and isomerisation of internal olefins with pinacolborane to yield terminal boronates in yields comparable to those obtained if O$_2$-treated RhCl(PPh$_3$)$_3$ was used.

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21. A solution of pinacolborane in THF (0.4 ml, 0.4 mmol) was injected into an oven-dried, nitrogen-purged and septum-capped quartz NMR tube. The solution was then analysed using ^{11}B NMR spectroscopy for purity. To this solution was added simultaneously, *trans*-4-octene (63 μl, 0.4 mmol) and RhCl(PPh$_3$)$_3$ (8 μmol, 7.4 mg) which had been dissolved in THF (0.5 ml) in a separate flame dried, nitrogen-flushed flask. The contents of the tube were shaken vigorously, vented under nitrogen and inserted into the microwave cavity. The sample was then irradiated with microwave energy (100 W) using a CEM discovery microwave reactor, for 20 min with concomitant cooling. The sample temperature was monitored by a non-contact, infrared sensor (located under the microwave cavity floor) and remained at 25 °C. The resulting orange-yellow solution was analysed by high-field ^{11}B NMR spectroscopy, which indicated a singlet at 34.3 ppm characteristic of the octyl-boronate ester (73%). The contents of the tube were subsequently quenched by addition of water (1 ml). The product was extracted with 3 × 2 ml ether and dried over MgSO$_4$. Flash column chromatography on silica gel with ethyl acetate/hexane mixture (2:98) and removal of

the solvent in vacuo afforded 2-octyl-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane. ^{11}B NMR (160 MHz; BF_3:OEt_2) δ 34.3 (s, B); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.71 (t, $J = 7.9$ Hz, 2H), 0.82 (t, $J = 5.6$ Hz, 3H), 1.19 (s, 12H), 1.20–1.24 (m, 10H), 1.32–1.39 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.7, 22.7, 23.1, 24.0, 24.8, 29.7, 30.1, 32.1, 82.7; MS (EI) m/z 241 ($M+H^+$, 40%), 225 (100), 224 (24), 183 (10), 127 (22), 97 (30), 69 (54); IR (Neat): 2960 (s), 1744 (s), 1376 (s), 1234 (s), 1146 (s), 1073 (s) cm^{-1}.

22. All glassware was thoroughly dried overnight in an oven at ca. 150 °C overnight. The glassware was further flame-dried by heating with a hot air gun under reduced pressure and allowed to cool under a stream of dry nitrogen, which was passed through a mixture of silica gel and 0.4 nm molecular sieves just prior to use. Glass syringes, cannulae, and needles were oven dried and stored in a desiccator (charged with a mixture of silica gel and 0.4 nm molecular sieves) prior to use. Disposable syringes and needles were stored in the desiccator before use, and they were discarded after single use. On assembling the glassware, all joints were wrapped with Teflon® tape, and were subsequently sealed with Parafilm 'M'® to ensure a closed system. ^{11}B NMR spectroscopy was utilised in order to identify the compounds as well as to monitor the progress of the reactions. ^{13}C and ^{1}H NMR spectroscopy and GC–MS were used to identify the hydroboration products.