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1,2-METALLATE REARRANGEMENTS OF α-ALKOXYVINYL BORATES

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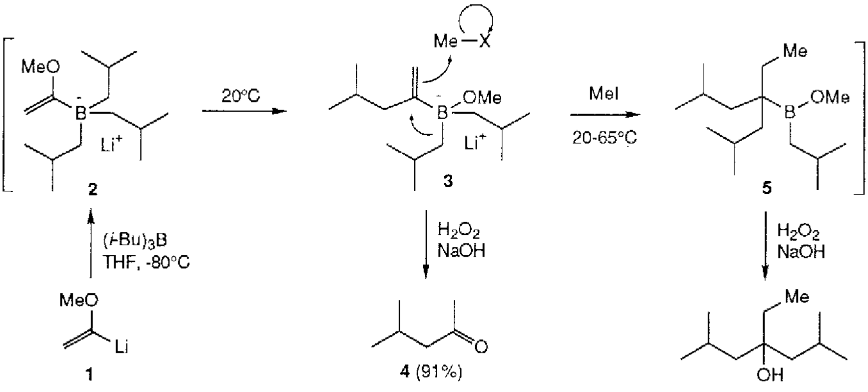
Abstract: α-Alkoxyvinyl borates derived from reaction of 5-lithio-2,3-dihydrofuran with trialkylboranes rearrange by two different mechanisms depending on the reaction conditions.

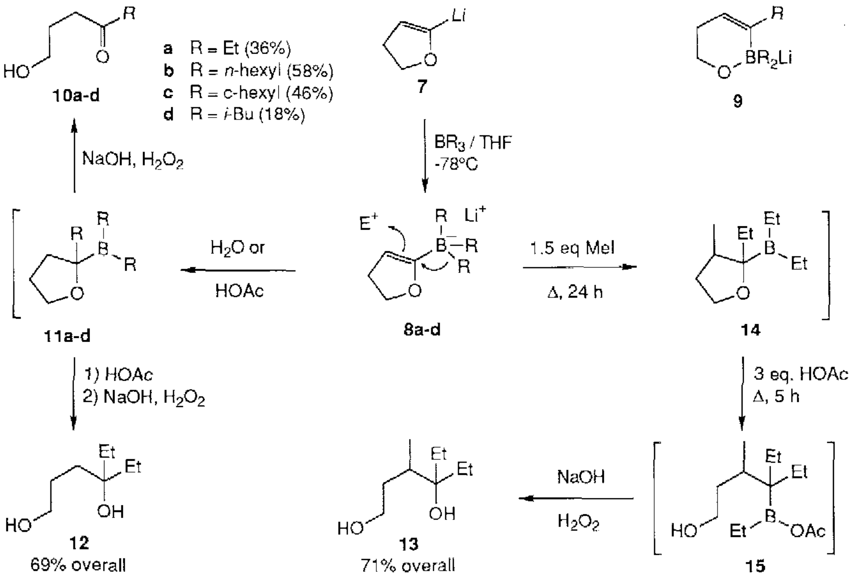
In 1976 Levy and Schwartz[1] suggested that the borate **2** generated at -80°C by reaction of α-methoxyvinyl-lithium (**1**) and tri-isobutylborane underwent a 1,2-alkyl shift on warming to room temperature to produce the alkenyl borate **3** (Scheme 1). The putative intermediate **3** was invoked to explain the formation of ketone **4** and tertiary alcohol **6**. Whilst oxidation of alkenyl boranes was well precedented, the ease and efficiency with which weak electrophiles such as alkyl halides induced a second 1,2-alkyl shift (**3** to **4**) was not and these results suggested electron density at the alkene terminus of **3** comparable to enamines. More recently Soderquist and Rivera[2] have shown that α-methoxyvinyl borates akin to **2** are stable at room temperature but that a 1,2-alkyl shift can be provoked by trimethylsilyl chloride. In this case, the silane co-ordinates to the methoxyl group in **2**, thus enhancing its nucleofugacity, and only then does rearrangement take place by 1,2-alkyl migration with concomitant loss of methoxytrimethylsilane. We now report independent evidence bearing on the stability and reactivity of alkoxyvinyl borates derived from 5-lithio-2,3-dihydrofuran which shows that 1,2-alkyl shifts can take place by two different mechanisms depending on the reaction conditions.



Scheme 1

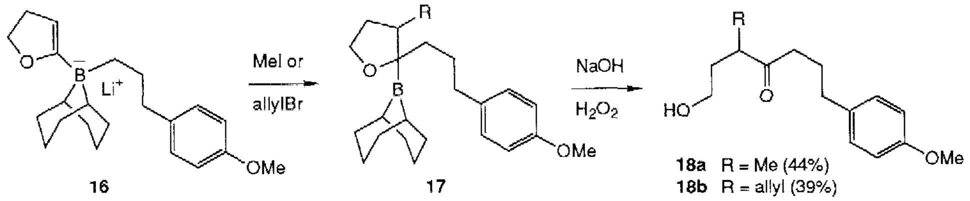
Addition of various trialkylboranes to a solution of 5-lithio-2,3-dihydrofuran **7** gave the borates **8a-d** which were then warmed to 20°C whereupon oxidative workup (Scheme 2) gave the hydroxyketones **10a-d**. Similarly, heating the borates **8a** with methyl iodide followed by HOAc and oxidative workup provided the tertiary alcohol **13**. We presumed that the borates **8a-d** rearranged on warming to give the alkenylborates **9** in accord with Levy's postulate and that these then underwent the observed transformations. However, all attempts to perform other reactions characteristic of alkenyl boranes (*vide infra*) using the putative intermediate

9 failed completely. These experiments suggested that the α-alkoxyvinyl borates **8a-d** were stable and that rearrangement to **9** was not taking place under the reaction conditions. Indeed, the borates **8a-d** could be heated at 65°C (THF) for 24 h without suffering any further change. Consequently the 1,2-alkyl shifts must have taken place by electrophilic attack on the borates **8a-d**; furthermore, the fact that rearrangement was induced by aqueous NaOH and MeI suggests that the borates **8a-d** were very susceptible to electrophilic attack at the alkene terminus.



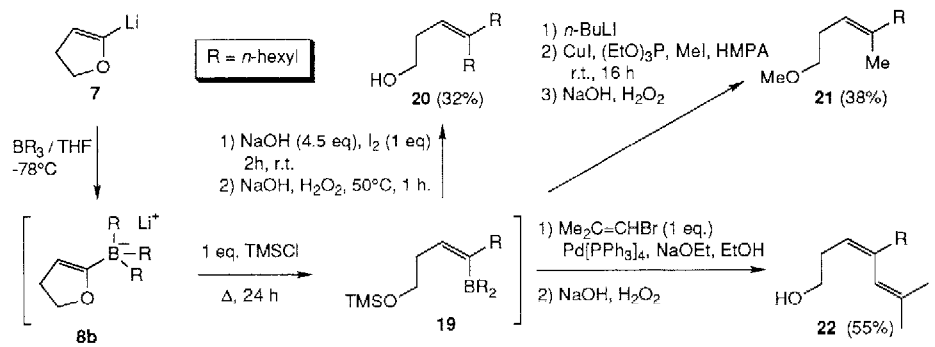
Scheme 2

The formation of the methylated tertiary alcohol **13** (Scheme 3) required a second 1,2-alkyl shift induced by reaction of intermediate **14** with HOAc. In order to prove that heating borates with alkyl halide was sufficient to induce a single 1,2-alkyl migration, we treated the α-alkoxyvinyl borate **16** with MeI and allyl bromide at 20°C for 16 h to induce alkylative rearrangement and then oxidised the intermediate **17** to give the hydroxyketones **18a,b** in modest yield.



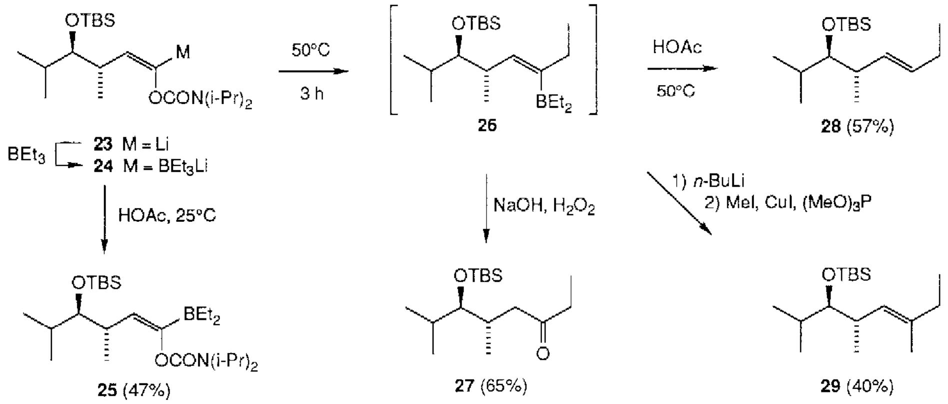
Scheme 3

Scheme 4 illustrates an alternative mechanism by which a 1,2-alkyl shift can be induced. When α-alkoxyvinyl borate **8b** was heated for 24 h in THF in the presence of 1 equivalent of the oxyphilic Lewis acid TMSCl, an intermediate **19** was generated which displayed chemistry typical of alkenylboranes[3]. Thus treatment of **19** with iodine followed by oxidative workup generated the trisubstituted alkene **20**. In addition, the "ate" complex derived from reacting **19** with one equivalent of *n*-BuLi transmetallated to an organocuprate which then coupled[4] with MeI to give the alkene **21** in 38% yield. Similarly, Suzuki coupling[5] converted **19** to the diene **22** in 55% yield. In both coupling reactions, a single stereoisomer was isolated.



Scheme 4

In an attempt to extend the scope of the borate rearrangements, we briefly examined the chemistry of the α-carbamoyloxy borate **24** (Scheme 5) which was readily prepared from the lithiated enol carbamate **23**[6,7]. Unlike the corresponding α-alkoxy borates, HOAc did not provoke rearrangment of **24**; instead protonolysis occurred to give the borane **25** as a stable entity isolated by column chromatography[8]. However, rearrangment did occur *in the absence of TMSCl* on heating **24** to 50°C for 3 h whereupon the alkenyl borane **26** was generated which displayed typical reactions (Scheme 5).



Scheme 5

In conclusion we have shown that cyclic α-alkoxyvinyl borates have remarkable thermal stability but they are very susceptible to electrophilic attack at the alkene terminus resulting in an easy 1,2-alkyl shift. On the other hand, the oxyphilic Lewis acid TMSCl induces a 1,2-alkyl shift by a different mechanism to give an alkenyl borane. Both modes of reactivity have counterparts in analogous metallate complexes of copper[9] and aluminium[10] with the borates being at the low end of the scale of reactivity. In fact the reactions described herein are much slower and less efficient with the corresponding dihydropyranyl borates.

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8. Compound **25** gave the following spectroscopic data: **IR** (film): 2937 s, 2903 s, 2882 s, 1626 s, 1496 s, 1474 s, 1388 m, 1371 s, 1253 m, 1156 m, 1036 s, 1006 m, 967 m, 904 m, 880 m, 864 m, 837 s cm^{-1}; **^{1}H-NMR** (270 MHz, $CDCl_3$) 4.58 (1H, d, J = 9.5), 4.03 (2H, qq, J = 6.8), 3.30 (1H, dd, J = 5.8, 2.7), 2.86 (1H, ddq, J = 9.5, 6.7, 1.2), 1.32 (12H, m), 1.01 (3H, d, J = 6.7), 0.93 (9H, s), 0.89 (3H, d, J = 6.8), 0.88 (3H, d, J = 7.0), 0.71 (6H, dt, J = 7.5, 2.0), 0.44-0.22 (4H, m), 0.07 (3H, s), 0.05 (3H, s); **^{13}C-NMR** (67.5 MHz, $CDCl_3$) 161.5 (s), 109.7 (d), 81.0 (d), 48.1 (d), 47.8 (d), 34.8 (d), 32.8 (d), 26.3 (q), 20.8 (q), 20.75 (q), 20.35 (q), 20.3 (q), 19.93 (q), 19.9 (q), 19.4 (q), 18.6 (s), 15.1 (bt), 9.6 (q), 9.5 (q), -3.67 (q), -3.64 (q); **LRMS** (CI): m/z 471 [$(M+NH_4)^+$, 1%], 454 [$(M+H)^+$, 100%], 438 [$(M-Me)^+$, 2%], 424 [$(M-Et)^+$, 60%], 339 [$(M+H-TBDMS)^+$, 1%], 322 [$(M-OTBDMS)^+$, 9%], 309 [$(M-OCONPr^i_2)^+$, 2%), 292 [$(M-OTBDMS-EtH)^+$, 2%], 268 (3%), 201 (8%), 184 (6%), 131 [$(OTBDMS)^+$, 2%], 128 [$(CONPr^i_2)^+$, 6%, 102 (7%); **HRMS**: found M^+=454.3889. Calculated for $C_{25}H_{53}BNO_3Si$ 454.3888.

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