Stereospecific Trisalkylation of Pentaborane(9) using Lithium Triethylhydridoborate

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Lithium triethylhydridoborate acts as a stereospecific trisalkylating agent toward B_5H_9 producing exclusively 2,3,4-triethylpentaborane(9), while lithium tri(s-butyl)hydridoborate produces only the monoalkyl product 2-(s-butyl)pentaborane(9).

Trialkylhydridoborates are among the strongest nucleophiles known. Lithium triethylhydridoborate, $LiEt_3BH$, for example, has been estimated to be 10 000 times more powerful as a nucleophile than lithium borohydride,[1] and it has been very useful in a number of hydridic reductions, including reductive displacement of halogens from alkyl halides,[1] reductive opening of epoxides,[2] and the reduction of transition metal carbonyls.[3]

We have found that while $LiEt_3BH$ may act as a super-nucleophile toward B_5H_9, its more spectacular action is as a stereospecific trisethylating agent, producing 2,3,4-triethylpentaborane(9), 2,3,4-$Et_3B_5H_6$, Figure 1, as the exclusive pentaborane product.

In a typical experiment 10 mmol of 1.0 M $LiEt_3BH$ in tetrahydrofuran (THF) was mixed with 12 mmol of B_5H_9 with warming from −78 °C to room temperature over several hours. High vacuum trap-to-trap distillation[4] of the volatile components so produced led to condensation of an unknown material in a −40 °C trap (23% yield). This material was identified as 2,3,4-$Et_3B_5H_6$ by ^{11}B and ^{1}H n.m.r. spectroscopy (Tables 1 and 2) and by high resolution mass spectroscopy: $^{12}C_6{}^1H_{21}{}^{11}B_5{}^+$, *m/z* 148.211 found; *m/z* 148.218 calc. N.m.r. analysis of the THF extract of the nonvolatile portion of the reaction mixture showed the presence of BH_4^- and $B_9H_{14}^-$ anions. In similar reactions using $Li(Bu^s)_3BH$ in THF solution, low yields (2.8%) of 2-$(Bu^s)B_5H_8$ were collected in a −69 °C trap. N.m.r. characterization data are in Tables 1 and 2.

The stereospecific formation of 2,3,4-$Et_3B_5H_6$ in the reaction of $LiEt_3BH$ with B_5H_9 leads us to suggest the possibility that a discrete previously undescribed reaction route is involved. We postulate that the reaction mechanism may involve addition of Et_3BH^- to the base of the B_5H_9 pyramid to form an intermediate complex of formula $Et_3B_6H_{10}^-$ which would be expected to be a hypho structure,[5] perhaps similar to its isoelectronic analogue, $B_6H_{10}(PR_3)_2$.[6] Such an intermediate complex would undoubtedly undergo ethyl group migration to adjacent boron atoms in order to relieve steric strain. Subsequent elision of BH_4^- would then form 2,3,4-$Et_3B_5H_6$ according to equation (1).

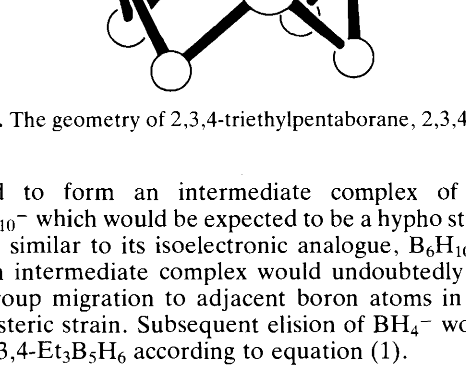

Figure 1. The geometry of 2,3,4-triethylpentaborane, 2,3,4-$Et_3B_5H_6$.

$$LiEt_3BH + B_5H_9 \xrightarrow{THF} 2,3,4\text{-}Et_3B_5H_6 + LiBH_4 \qquad (1)$$

Experiments in which large excesses of B_5H_9 or $LiEt_3BH$ were used also produced 2,3,4-$Et_3B_5H_6$ as the only significant pentaborane product. When excess of $LiEt_3BH$ was employed, significant quantities of Et_3B were formed. If the

Table 1. ^{11}B N.m.r. spectral data.

Compound	B Resonance	Chemical shift[a]	Multiplicity; coupling constant[b]
2,3,4-$Et_3B_5H_6$	B(3)	+2.0	s
	B(2,4)	−2.5	s
	B(5)	−19.5	d; 151
	B(1)	−49.6	d; 156
2-(Bu^s)B_5H_8	B(2)	+3.9	s
	B(3,5)	−15.0	d; 167
	B(4)	−19.4	d; 163
	B(1)	−53.3	d; 175

[a] In p.p.m. referenced to $BF_3 \cdot OEt_2$, negative values upfield; C_6D_6 solvent. [b] Coupling constant in Hz; s = singlet; d = doublet.

Table 2. ^{1}H N.m.r. spectral data.

Compound	H(–B) Resonance	Chemical shift[a]	Multiplicity; coupling constant[b]
2,3,4-$Et_3B_5H_6$	H(5)	+2.25	q; 155
	H(1)	+0.73	q; 166
	H(6,7)	−1.37	br.
	H(8,9)	−2.08	br.
2-(Bu^s)B_5H_8	H(3,4,5)	+2.38	q; 168
	H(1)	+0.93	q; 173
	H(6,9)	−2.05	br.
	H(7,8)	−2.69	br.

[a] Referenced to Me_4Si, negative values upfield, C_6H_6 solvent. [b] Coupling constants in Hz; q = quartet; br. = broad.

ethyl substitution reaction occurs *via* any mechanism that requires co-ordination of the Et_3BH^- to the pentaborane molecule it is unlikely that a second Et_3BH^- group could easily co-ordinate to the 2,3,4-$Et_3B_5H_6$ product. As no higher-ethylated pentaboranes were observed in this study, it would appear that suitable reaction pathways between 2,3,4-$Et_3B_5H_6$ and $LiEt_3BH$ are not available under the stated reaction conditions.

As $LiEt_3BH$ is a strong hydride donor, it would be expected to react with B_5H_9 to form $B_5H_8^-$ or $B_5H_{10}^-$ by proton abstraction or hydride addition, respectively. Subsequent alkyl exchange between free BEt_3 and the borane anion could produce the observed 2,3,4-$Et_3B_5H_6$ product. In attempts to verify this we have found no evidence for reaction between BEt_3 and preformed KB_5H_{10}[7] in Me_2O or LiB_5H_8[8] in Et_2O.

In experiments employing Li(Bu^s)$_3$BH, the only B_5H_9 derivative produced was the monosubstituted 2-(Bu^s)B_5H_8, along with large quantities of (Bu^s)$_3$B. While steric factors might be important in the selective formation of 2-(Bu^s)B_5H_8, there would presumably be no steric restriction on 2,4-substitution. The absence of any 2,4-substitution products indicates that electronic effects control the substitution reaction pathways.

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