Lithium Triethylborohydride-promoted Hydroboration of Alkenes with Dialkoxyboranes

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In the presence of a catalytic amount of lithium triethylborohydride ($LiBEt_3H$) the hydroboration of alkenes with dialkoxyboranes is promoted markedly to provide the hydroboration products almost quantitatively under mild reaction conditions.

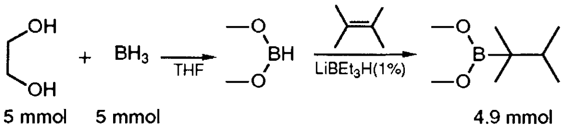
As catecholborane[1,2] and dialkoxyboranes[3,4] hydroborate alkenes at a very slow rate they have so far been little used as hydroborating reagents for alkenes. We recently reported that the presence of a catalytic amount of $LiBH_4$ enhanced the rate of hydroboration of alkenes by catecholborane.[5] We now report that dialkoxyboranes in the presence of 1% $LiBEt_3H$ hydroborate alkenes under mild reaction conditions.

Although in the absence of $LiBEt_3H$ the hydroboration of hex-1-ene with dibutoxyborane $(BuO)_2BH$† was very sluggish affording only 17% of hexan-1-ol at 20 °C for 20 h, in the presence of a catalytic amount of $LiBEt_3H$, less than 1% (procedure A), it was promoted markedly affording 72% yield of a mixture of hexan-1-ol and hexan-2-ol in a ratio of 95 : 5. A

Table 1 Hydroboration of alkenes with dialkoxyboranes in the presence of $LiBEt_3H$[a]

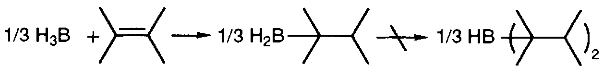
ROH for $(RO)_2BH$ (5 mmol)	Alkene (5.5 mmol)	*T*/°C	*t*/h	Product	Yield (%)[b]
Butan-1-ol[c]	Hex-1-ene	20	20	Hexan-1-ol	17[e]
				Hexan-2-ol	trace[e]
		20	5	Hexan-1-ol	95
				Hexan-2-ol	5
	Cyclohexene	20	5	Cyclohexanol	90
	1-Methylcyclohexene	20	5	*trans*-2-Methylcyclohexanol	95
	2,3-Dimethylbut-2-ene	50	20	2,3-Dimethylbutan-2-ol	73
Propan-2-ol[c]	Hex-1-ene	20	20	Hexan-1-ol	51
				Hexan-2-ol	3
		50	2	Hexan-1-ol	94
				Hexan-2-ol	6
	1-Methylcyclohexene	50	2	*trans*-2-Methylcyclohexanol	99
Ethylene glycol[d]	2,3-Dimethylbut-2-ene	50	2	2,3-Dimethylbutan-2-ol	98

[a] The reactions were carried out by successive additions of 0.05 mmol of $LiBEt_3H$ in THF (1 mol dm^{-3}), 10 mmol of alcohol and 5.5 mmol of alkene to 5 mmol of BH_3 in THF (0.5 mol dm^{-3}). [b] Determined by GLC and based on BH_3. [c] ROH was added to BH_3 in THF at 20 °C. [d] 5 mmol of ethylene glycol was added to BH_3 in THF at 0 °C. [e] In the absence of $LiBEt_3H$.



(2)

$$(RO)_2BH \longrightarrow 2/3\ (RO)_3B + 1/3\ BH_3$$



(3)

further study on the promotion revealed that an addition of $LiBEt_3H$ in the dibutoxyborane-forming stage (procedure B) also promoted the hydroboration as well as the formation of dibutoxyborane† providing a quantitative yield of hexanols [eqn. (1)].

By this procedure B, hex-1-ene, cyclohexene and 1-methylcyclohexene were hydroborated quantitatively suggesting that the present reaction was widely applicable to the hydroboration of mono-, di- and tri-substituted ethenes. However, in the case of 2,3-dimethylbut-2-ene, a tetra-substituted ethene whose $LiBH_4$-promoted hydroboration with catecholborane was quantitative, the quantitative hydroboration could not be achieved by using either procedure A or B. Similar results were obtained by using diisopropoxyborane $(i\text{-}C_3H_7O)_2BH$,† though the hydroboration conditions were a little different (50 °C, 2 h).

The reaction of ethylene glycol with BH_3 in tetrahydrofuran (THF) in a molar ratio of 1 : 1 proceeds rapidly in the presence or in the absence of $LiBEt_3H$ providing a dialkoxyborane-like compound having at least one hydrogen atom on the boron atom though its structure has not be clarified. An addition of alkenes to this reaction mixture provided the hydroboration products in high yield. By applying procedure A this solution provided the hydroboration product from 2,3-dimethylbut-2-ene nearly quantitatively under mild reaction conditions [50 °C, 2 h; eqn. (2)]. These results are shown in Table 1.

It has been reported that one mole of dimethoxyborane decomposed easily to provide two third mole of trimethoxyborane and one third mole of BH_3.[6] Thus, there was a possibility that in the present reaction the alkenes were hydroborated not by dialkoxyboranes, but by BH_3 formed during the reaction. In such cases the yield of 2,3-dimethylbutan-2-ol must be below 33% based on starting dialkoxyborane.[7] Accordingly, nearly quantitative yield, 98%, obtained as above suggested that this hydroboration proceeded by a direct addition of dialkoxyborane to the alkenic double bond to provide dialkoxyalkylborane [see eqn. (3)].

Indeed, in the ^{11}B NMR spectrum of the above reaction mixture revealed that about 97% of the boron atom existed as a dialkoxyalkylborane (singlet, δ 35.4 from $BF_3{\cdot}Et_2O$). However, surprisingly, the ^{11}B NMR spectrum of the reaction mixture obtained by the reaction of hex-1-ene with $(BuO)_2BH$ showed that about 30% of the boron atom was present as $(Hex)_3B$ (singlet, δ 83 from $BF_3{\cdot}Et_2O$) and only about 10% of $(BuO)_2BHex$ (singlet, δ 32 from $BF_3{\cdot}Et_2O$) was formed.

Although further studies including examinations by ^{11}B NMR are needed to rationalize these results, the present reaction seems to be applicable for the preparation of dialkoxyalkylboranes from sterically hindered alkenes and provides a new hydroboration methodology.

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