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# Borane-catalyzed hydroboration of substituted alkenes by lithium borohydride or sodium borohydride

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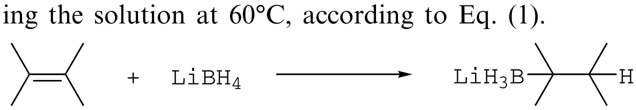
**Abstract**—In the presence of a catalytic amount of $BH_3{\cdot}Me_2S$, $TiCl_4$ or $Me_3SiCl$, $LiBH_4$ or $NaBH_4$ are capable of hydroborating alkenes by following the unusual order of decreasing reactivity: tetramethylethylene > 1-methylcyclohexene > cyclohexene; the key step of the catalytic cycle is the exchange reaction between $LiBH_4$ and the mono- or dialkylboranes resulting from hydroboration of the more substituted alkenes with $BH_3$.


Alkenes are reputed to be inert towards alkali metal borohydrides[1] unless these nucleophilic species are used in conjunction with a carboxylic acid or ester[2–4] or a transition metal compound.[2,5–7] Such reagent systems, in particular the $NaBH_4$–AcOH[3] and the $LiBH_4$–$TiCl_x$ ($x=3$, 4)[6] combinations, act as a source of borane species which are capable of hydroborating alkenes, and the reactivity of the C=C double bonds follows the sequence mono- > di- > tri- > tetra-substituted, as is invariably observed with hydroborating agents. However, we found that alkenes can be hydroborated with $LiBH_4$ in the presence of $UCl_4$, $ZrCl_4$ or $NdCl_3$,[8] following the opposite order of reactivity, i.e. tetramethylethylene > 1-methylcyclohexene ≫ 2-methylpropene or 1-hexene (no reaction). Subsequent studies on the mechanism of this intriguing reaction have revealed that $LiBH_4$ is capable of hydroborating the more substituted alkenes in the presence of a catalytic amount of $BH_3$.

Despite the generally accepted idea that alkenes do not react with $LiBH_4$, we carried out a control experiment with tetramethylethylene. No reaction was observed at room temperature between $Me_2C{=}CMe_2$ and $LiBH_4$ in THF, but the slow formation of lithium thexylborohydride $LiBH_3R$ ($R=CMe_2CMe_2H$) did occur upon heating the solution at 60°C, according to Eq. (1).




(1)

By using a 10-fold excess of $LiBH_4$ (0.2 M), 43% of the alkene was transformed into $LiBH_3R$ after 48 h.[9] Under the same conditions, practically no reaction was observed with 1-methylcyclohexene. Further, we found that not only were the mono- and di-substituted alkenes inert towards $LiBH_4$ but they also prevented the reaction of tetramethylethylene. Thus, hydroboration of the latter (0.02 M in THF) with $LiBH_4$ (0.2 M) did not occur in the presence of 1 mol equiv. of 1-hexene.

Involvement of free borane species in the hydroboration process seemed at first unlikely, considering that these species would react preferentially with the less substituted alkenes. However, striking new facts emerged when the reactions were performed in the presence of small amounts of $BH_3$; these are illustrated in Figure 1 which represents the rate of hydroboration of various alkenes.

Treatment of 1-hexene (0.2 M in THF) with 1 equiv. of $LiBH_4$ and 0.05 equiv. of $BH_3{\cdot}Me_2S$ led to the formation of the trialkylborane B($n$-hexyl)$_3$, in 15% yield with respect to 1-hexene;[9] the alkene was thus normally hydroborated with the added quantity of $BH_3$, and $LiBH_4$ had no effect on this transformation. Surprisingly, under the same conditions, tetramethylethylene was totally converted into lithium thexylborohydride; reaction (1) was then complete after 6 h at 20°C. Addition of 5 mol% of $BH_3{\cdot}Me_2S$ to the 1:1 mixture of $LiBH_4$ and cyclohexene or 1-methylcyclohexene also started the hydroboration reaction of these di- and trisubstituted alkenes; after 20 h at 20°C, their conversion was equal to 28 and 55%, respectively.[9] Similar

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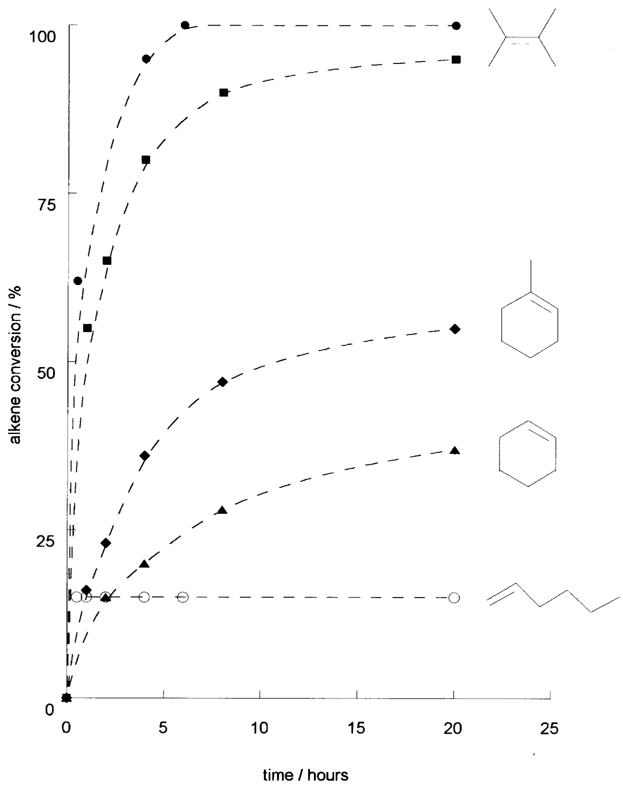
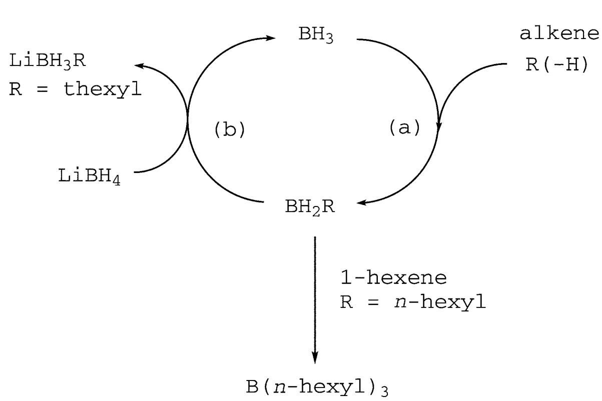



**Figure 1.** Rate of hydroboration of various alkenes (0.2 M in THF) with 1 equiv. of $LiBH_4$ in the presence of 0.05 equiv. of $BH_3{\cdot}Me_2S$ or $Me_3SiCl$ (reaction of $Me_2C{=}CMe_2$ with $NaBH_4$ and $BH_3{\cdot}Me_2S$ is denoted by ■)

results were obtained when $NaBH_4$ was used in place of $LiBH_4$ but the reactions were a little slower, that of tetramethylethylene being complete after 20 h at 20°C.

These observations clearly revealed that $BH_3$ plays a catalytic role in the hydroboration of alkenes with $LiBH_4$. The reactions can be accounted for by the catalytic cycle shown in Scheme 1, with the description of the behavior of 1-hexene and tetramethylethylene which represent limiting cases. Classical hydroboration of the C=C double bond with $BH_3$ (step a) would afford the trialkylborane B($n$-hexyl)$_3$ from 1-hexene, and the




**Scheme 1.** Proposed catalytic cycle for the hydroboration of alkenes with $LiBH_4$ in the presence of $BH_3$.

monoalkylborane $BH_2$(thexyl) from tetramethylethylene. The distinct reactivity of mono- and tetra-substituted alkenes in their reactions with borane species is well documented.[1b,10] The second step (b), operative only in the case of $Me_2C{=}CMe_2$, would be the exchange reaction between $LiBH_4$ and $BH_2R$ to give $LiBH_3R$ (R = thexyl) and regeneration of $BH_3$. That $LiBH_4$ is transformed into $LiBH_3R$ in the presence of $BH_2R$ (R = thexyl) but does not react with B($n$-hexyl)$_3$ was verified in separate experiments. Also in agreement with the proposed mechanism, hydroboration of $Me_2C{=}CMe_2$ with $LiBH_4$ was found to occur upon addition of $BH_2$(thexyl), due to the formation of $BH_3$ from the exchange reaction, while B($n$-hexyl)$_3$ had no effect.

Since reaction of $BH_3$ with 1-hexene is faster than with tetramethylethylene, it was not surprising that addition of 5 mol% of $BH_3{\cdot}Me_2S$ to an equimolar mixture of these two alkenes and $LiBH_4$ led to the sole production of B($n$-hexyl)$_3$, in 15% yield, without inducing the hydroboration of the tetrasubstituted alkene. The slow conversions of cyclohexene and 1-methylcyclohexene indicate that the corresponding dialkylboranes, which are the expected products of hydroboration of these alkenes with $BH_3$,[1b,10] also undergo the exchange reaction with $LiBH_4$, with a lower rate than the monoalkylboranes. The distinct behavior of substituted alkenes in their reaction with $LiBH_4$ in the presence of a catalytic amount of $BH_3$ is thus determined by both steps of the catalytic cycle: (a) the hydroboration with $BH_3$ which gives the less substituted borane species from the more substituted alkenes, and (b) the exchange reaction between $LiBH_4$ and the borane species which occurs only with the less substituted mono- and dialkylboranes.

The above results strongly suggest that reaction (1) is due to the presence of a trace of $BH_3$ which would result from decomposition of $LiBH_4$, possibly induced by some impurity. However, no borane species could be detected after refluxing a THF solution of $LiBH_4$ for 5 days, and the trialkylborane B($n$-hexyl)$_3$ was not observed after treatment of 1-hexene with $LiBH_4$ under the same conditions. Further studies are in progress to identify the nature of the active species in reaction (1).

Since metal halides like $SnCl_4$,[5] $TiCl_4$[6] and $CoCl_2$[7] are known to react with $LiBH_4$ or $NaBH_4$ to give stoichiometric amounts of $BH_3$, it was expected that addition of a catalytic quantity of metal halide to a mixture of $LiBH_4$ and alkene would have the same effect as $BH_3$ in the hydroboration reactions. Indeed, treatment of $Me_2C{=}CMe_2$ with 1 equiv. of $LiBH_4$ in the presence of 1 mol% of $TiCl_4$ gave lithium thexylborohydride in almost quantitative yield after 48 h at 20°C, while the same reaction with 1-hexene afforded B($n$-hexyl)$_3$ in 3% yield. It has also been reported that $Me_3SiCl$ reacts with $LiBH_4$ or $NaBH_4$ to give $BH_3$,[11] and the $Me_3SiCl$–$PhCH_2NEt_3BH_4$ reagent system is capable of hydroborating alkenes.[12] In line with these previous studies, the hydroboration of $Me_2C{=}CMe_2$ with $LiBH_4$ or $NaBH_4$

could also be promoted by a catalytic amount of the chlorosilane; the same results were obtained by using either $BH_3 \cdot Me_2S$ or $Me_3SiCl$ as the catalyst. From a practical and economical point of view, it is interesting that the hydroboration of substituted alkenes by the combinations of $LiBH_4$ or $NaBH_4$ with $TiCl_4$ or $Me_3SiCl$, which are useful hydroborating reagents, can be performed with only a catalytic quantity of the metal halide or chlorosilane.

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