

Hydroboration of Bis(trimethylsilyl)ethyne.

New Aspects of Hydroboration

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The hydroboration of bis(trimethylsilyl)ethyne, $\text{Me}_3\text{Si}-\text{C}\equiv\text{C}-\text{SiMe}_3$ **1**, with 9-borabicyclo [3.3.1] nonane (9-BBN) gives first the expected (*Z*)-alkene **5** which rearranges, without UV irradiation, after several days quantitatively into the (*E*)-alkene **6**. Heating of **6** in the presence of a further equivalent of **1** leads, again almost quantitatively, to an allene, the 1,1,4,4-tetrakis(trimethylsilyl)-4-[9-(9-borabicyclo[3.3.1]nonyl)]buta-1,2-diene **8**. Reactive structures arising from π - σ delocalisation involving the boryl group are proposed to be responsible both for the *cis/trans*-isomerisation and the allene formation. It is suggested that analogous structures may explain the previously observed formation of allenes **9** and **10**, tin-analogues of **8**. The structures of **5**, **6** and **8** in solution follow from a consistent set of NMR data (^1H , ^{11}B , ^{13}C , ^{29}Si NMR), and the solid-state structure of **8** was confirmed by X-ray analysis.

Key words: Alkynes, Alkenes, Allenes