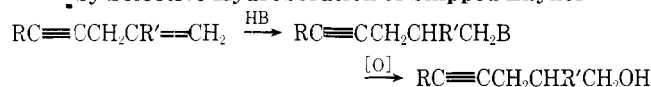


Table II. Acetylenic B-alkyl-9-borabicyclo[3.3.1]nonanes by Selective Hydroboration of Skipped Enynes

R	R'	% yield	
		organoborane ^a	alcohol ^b
<i>n</i> -C ₃ H ₇	H	95	93 ^c (84) ^d
<i>n</i> -C ₆ H ₁₃	H	98	92 ^c
<i>n</i> -C ₆ H ₁₃	CH ₃	100	98 ^c
C ₆ H ₅	H	94	86 ^c

^a Crude yield (5.0-mmol scale) after evaporation of solvent to constant weight. ^b Comparable yields were obtained either by concentrating the organoborane and then oxidizing with alkaline H₂O₂ or by direct oxidation of the hydroboration mixture. ^c Semi-isolated yield. After extractive workup and drying, internal standard was added for GLC analysis. ^d Isolated yield on a 25-mmol scale as follows. A solution of 25 mmol of 9-BBN (0.5 M) in THF was added over 2 min (0 °C, under argon) to a stirred solution of 25 mmol of 1-octen-4-yne (Farchan Research Laboratories) in 10 mL of THF. The reaction mixture was warmed to room temperature and stirred for 60 min. Oxidation was carried out with alkaline hydrogen peroxide.⁸ The THF layer was dried with K₂CO₃ and distilled to yield 2.65 g (84%) of 4-octyn-1-ol, bp 83–84 °C (3 mm), *n*_D²⁰ 1.4574, pure by GLC on polar and nonpolar columns.

of Table I in ref 5, without the necessity of alkyne blocking agents.⁶

Formation of acetylenic B-alkyl-9-BBN derivatives has been similarly achieved by hydroboration of readily available⁷ allylic acetylenes with 9-BBN; hydroboration appeared highly selective in either hexane or THF, as determined by oxidation and GLC analysis; there was no evidence for enhanced hydroboration of the triple bond in the acetylenic B-alkyl-9-BBN products. Evaporation of the solvent yielded the organoborane as a clear, pale yellow oil in quantitative crude yield.

The organoboranes were converted to alcohols via conventional oxidation with alkaline hydrogen peroxide. These results are summarized in Table II.

In view of the reports the B-alkyl-9-BBN undergoes selective transfer of the alkyl groups in various organoborane reactions,⁹ these results appear of considerable synthetic potential. We are currently examining such applications.

References and Notes

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