Novel Synthesis of an ω-Alkynylorganometallic Reagent *via* Triple Bond Isomerization with Potassium 3-Aminopropylamide: ω-(9-Borabicyclo[3.3.1]nonan-9-yl)alkl-1-ynes

By Charles Allan Brown*
(*Department of Molecular and Chemical Dynamics, I.B.M. Research Laboratory* K34-281, 5600 *Cottle Rds., San Jose, California* 95193
and Ei-ichi Negishi
(*Department of Chemistry, Syracuse University, Syracuse, New York* 13210)

Summary Isomerization of 1-(9-borabicyclo[3.3.1]nonan-9-yl)oct-4-yne, readily prepared by hydroboration of oct-1-en-4-yne with 9-borabicyclo[3.3.1]nonane and 2·5—3·0 equiv. of potassium 3-aminopropylamide, yields quantitatively 1-(9-borabicyclo[3.3.1]nonan-9-yl)oct-7-yne, which undergoes typical organoborane, reactions such as oxidation and alkyltransfer to α-bromoketones.

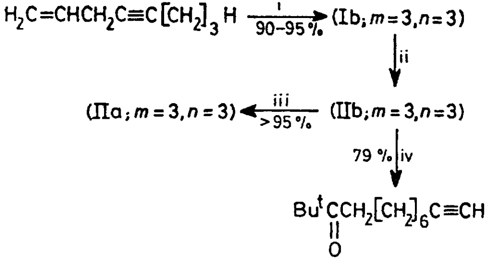
Potassium 3-aminopropylamide (KAPA) is an exceptionally active catalyst for prototropic reactions including multipositional isomerization of alkynes and alkynols (*e.g.*, I → II, X = H or OH).[1,2] Extensions to other functionalized alkynes [*e.g.*, I, X = –CO_2H, –C(O)–, –OMe, *etc.*] are

$$\underset{\text{(I)}}{X[CH_2]_m\,C{\equiv}C[CH_2]_nH} \qquad \underset{\text{(II)}}{X[CH_2]_{m+n}C{\equiv}CH}$$

a, X = OH
b, X = BR_2

generally marginal (except tertiary amines) as the randomly migrating triple bond becomes involved with the functions.[2a,3a]

The metal–carbon bond of organoboranes resists cleavage by aqueous acids and all bases,[3,4] yet possesses remarkable versatility in synthetic reactions.[5] Preparation and isomerization of organoboranes containing a triple bond has been realized in high yield; the ω-alkynylorganoboranes undergo typical organoborane reactions such as oxidation and alkyl transfer from boron to carbon as shown in the Scheme.†



Scheme. i, R_2BH, THF, 0 °C, 3 h; ii, 2·5—3·0 KAPA, 0—20 °C, 1 h; iii, H_2O_2, NaOH; iv, $Bu^tC(O)CH_2Br$, Bu^tOK. R_2BH = 9-Borabicyclo[3.3.1]nonane.

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† All new compounds gave satisfactory i.r., n.m.r. and analytical data. Borane intermediates were characterized by i.r. and n.m.r. spectroscopy and by oxidation to known alcohols.

Hydroboration of oct-1-en-4-yne‡ with 9-borabicyclo-[3.3.1]nonane[6] in tetrahydrofuran (THF) at 0 °C proceeds smoothly and selectively to give (Ib; $m = 3$, $n = 3$); only traces of the octenyne remained after 3 h, and no evidence was observed for attack on the triple bond. As THF is attacked by KAPA, (Ib) was isolated either by evaporation of solvent under reduced pressure at 0—20 °C or by vacuum distillation (Ib, $m = 3$, $n = 3$; b.p. 96—100 °C at 0·06 mmHg). Isomerization was performed by addition of 5·0 ml of a 1·0M solution of organoborane in benzene to 12·5—15 ml of 1·0M KAPA at 0—20 °C, followed by stirring for 1 h and then by dilution with 30 ml of water and 15 ml of benzene. Compound (IIb; $m = 3$, $n = 3$) was isolated from the benzene solution by evaporation under reduced pressure or by complete vacuum distillation (b.p. 90—94 °C at 0·06 mmHg). Complete isomerization was achieved as determined by i.r. and n.m.r. spectroscopy and g.l.c. analysis after oxidation. The oxidations[7a] and the alkylation of α-bromopinacolone[7b] were performed according to published procedures. Hydroboration and isomerization of undec-1-en-4-yne‡ were accomplished similarly.

In separate experiments we have observed that dialkylalk-1-ynylboranes ($R_2BC{\equiv}CR^2$) and trialkylalk-1-ynyl borates ($[R^1_3BC{\equiv}CR^2]^-$) are immediately cleaved by KAPA liberating alk-1-ynes. No formation of alk-1-yne was observed in the isomerization of (Ib), indicating that the random triple bond migration never proceeds as far as the 1-position.

E.N. is an N.S.F. Summer Faculty Visitor at the I.B.M. Research Laboratory, San Jose.

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‡ Available from Farchan Research Laboratories, Willoughby, Ohio. These and similar alkenynes have been prepared in our laboratory in high yield by direct reaction of lithium acetylides with allyl bromide in THF (12—18 h, reflux).

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