consisted of extraction with saturated potassium carbonate, drying of the organic phase, and the removal of the solvent under reduced pressure. The almost pure residue (which, however, contains traces of selenium compounds) was purified by chromatography on silica gel. For example, *N*-nitrosodiethylamine was converted to ethylvinylnitrosamine in 71% overall isolated yield. This method is clearly the most costly, but has the virtue of being a general one, if the nitrosamine is symmetrical, and offers the possibility of preparation of a wide variety of α,β-unsaturated nitrosamines. Table I lists some representative vinylic nitrosamines which were prepared by one or more of the three methods.

The unsaturated nitrosamines are very interesting entities with a very rich chemistry, on which we will soon report. Most nitrosamines are potent carcinogens,[8] and the unsaturated materials are unlikely to be exceptions. These materials should be handled with extreme caution.

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Selective Hydroboration of Double Bonds in the Presence of Triple Bonds by 9-Borabicyclo[3.3.1]nonane. New Route to Acetylenic Organoboranes and Alcohols

Summary: Hydroboration of acetylenes with 9-borabicyclo[3.3.1]nonane is slow compared to hydroboration of structurally similar olefins, in direct contrast to the relative ease of hydroboration with other dialkylboranes. This unexpected reactivity allows clean selective hydroboration of double bonds in the presence of triple bonds and formation of acetylenic organoboranes directly from readily available allylic acetylenes.

Sir: In connection with studies of facile triple bond migrations catalyzed by the potassium 3-aminopropylamide hyperbase system[1] it was observed that carbinols and the organoborane moiety allowed migration of triple bonds to the opposite chain terminus in high yield (eq 1).[2]

$$\underset{\text{I}}{X(CH_2)_nC{\equiv}C(CH_2)_mH} \rightarrow \underset{\text{II}}{X(CH_2)_{m+n}C{\equiv}CH} \qquad (1)$$

$$\text{a, } X = HOCH_2,\ HOCR_2$$

$$\text{b, } X = R_2B$$

We desired a convenient route to acetylenic organoboranes in which the triple bond was isolated from the boron, as alkynylboranes (Ib, $n = 0$) are readily cleaved by the base.[3]

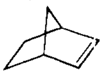
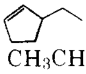
Hydroboration of nonconjugated enynes (I, $n = 1$, X = vinyl) appeared attractively simple; however, dialkylboranes were generally found to be more sluggish toward olefins than toward alkenes.[4] Recently, 9-borabicyclo[3.3.1]nonane (9-BBN) has been shown to exhibit relative reactivities toward alkenes which suggest a relatively electron-deficient transition state in hydroboration [compared to bis(3-methyl-2-butyl)borane].[5] This suggested the possibility of altered relative reactivity of alkynes and alkenes in hydroboration with 9-BBN.

In fact, 9-BBN is exceptionally sluggish in the hydroboration of 1-heptyne; mixtures of 1-heptyne and R_2BH (0.5 M in each in THF, 25 °C) show about 95% reaction of 1-heptyne in 1 min with dicyclohexylborane or bis(3-methyl-2-butyl)boranes but only 2% reaction with 9-BBN in the same time.

Addition of 0.05 mol of 9-BBN to a THF solution containing 0.05 mol each of 1-heptyne and 1-octene showed that when 9-BBN was completely consumed, nearly six times as much alkene had reacted as alkyne; bis(3-methyl-2-butyl)borane shows reversed selectivity.[4c] Disubstitution or conjugation of the triple bond produced almost complete selectivity for reaction of 9-BBN with the 1-alkene.

The scope of these unusual "reversed" selective hydroborations was probed with a series of alkene/alkyne mixutes; representative examples are shown in Table I. From these data we conclude that synthetically useful selective hydroborations of double bonds in the presence of dialkyl (or conjugated) alkynes can be achieved for all of the structures in the left half

Table I. Selective Hydroborations of Alkene–Alkyne Mixtures with 9-BBN at 25 °C[a]

substrates		% residual substrate[b]		selectivity ratio[c]	alkene
alkene	alkyne	alkene	alkyne	alkene/alkyne	reactivity[d]
$H_2C{=}CH\text{-}n\text{-}C_6H_{13}$	$HC{\equiv}C\text{-n-}C_5H_{11}$	15	85	5.7	1.1
$H_2C{=}CH\text{-}n\text{-}C_8H_{17}$	$HC{\equiv}CC_6H_5$	2	98	50	1.1
$H_2C{=}C(CH_3)(C_2H_5)$	$CH_3C{\equiv}C\text{-}n\text{-}C_5H_{11}$	<1	>99	>100	≃2.3
$H_2C{=}C(CH_2)_5$	$CH_3C{\equiv}C\text{-}n\text{-}C_5H_{11}$	<1	>99	>100	≃2.3
	$CH_3C{\equiv}C\text{-}n\text{-}C_5H_{11}$	<1	>99	>100	1.5
$H_2C{=}CH\text{-}n\text{-}C_6H_{13}$	$C_2H_5C{\equiv}CC_2H_5$	2	98	50	1.1
	$CH_3C{\equiv}C\text{-}n\text{-}C_5H_{11}$	14	86	6.1	≃0.65
$CH_3CH{=}C(CH_3)_2$	$C_2H_5C{\equiv}CC_2H_5$	55	45	0.82	0.0086
Z-$CH_3CH{=}CH\text{-}i\text{-}C_3H_7$	$C_2H_5C{\equiv}CC_2H_5$	65	35	0.54	0.0061

[a] Addition of 9-BBN solution in THF or in hexane to a stirred solution of substrates in THF. [b] GLC analysis with internal standard after 4–6 h (completed reaction) using polymethyl siloxane liquid phase. Room temperature injector used to prevent organoborane pyrolysis. [c] Based on alkene reacted/alkyne reacted. [d] Derived or estimated from Table I in ref 5.

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

$$\mathrm{RC{\equiv}CCH_2CR'{=}CH_2} \xrightarrow{\mathrm{HB}} \mathrm{RC{\equiv}CCH_2CHR'CH_2B} \xrightarrow{[\mathrm{O}]} \mathrm{RC{\equiv}CCH_2CHR'CH_2OH}$$

R	R′	% yield organoborane[a]	 alcohol[b]
n-C_3H_7	H	95	93[c] (84)[d]
n-C_6H_{13}	H	98	92[c]
n-C_6H_{13}	CH_3	100	98[c]
$C_6H_5^-$	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 H_2O_2 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 K_2CO_3 and distilled to yield 2.65 g (84%) of 4-octyn-1-ol, bp 83–84 °C (3 mm), $n^{20}{}_D$ 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 available[7] 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.

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