mixture was stirred for 1 h at 25 °C. The solvent, excess MeOH, and the HCl generated in the reaction were removed by using a water aspirator, and the resulting product, dimethyl *n*-hexylboronate, was distilled under reduced pressure: yield 3.3 g (83%), bp 84–86 °C (35 mmHg).

The methanolysis of $RBCl_2$ or $RBCl_2{\cdot}SMe_2$ can be carried out by following this procedure, and the methyl ester of alkylboronic acids can be isolated in good yields.

Methanolysis of Cyclopentyldibromoborane–Dimethyl Sulfide. The usual experimental setup was employed for the hydroboration of 8.8 mL (100 mmol) of cyclopentene with 12.8 mL (100 mmol) of $HBBr_2{\cdot}SMe_2$ in 75 mL of CH_2Cl_2. The reaction mixture was heated under reflux for 5 h. The flask was cooled to 0 °C, 44.5 mL of 4.5 M solution of NaOMe in MeOH (200 mmol) was added, and the mixture was stirred for 2 h at 25 °C. The solvent was removed under vacuum, and the product, dimethyl cyclopentylboronate, 10.5 g (74% yield), bp 76–78 °C (40 mmHg), was obtained as a colorless liquid.

The methanolysis of $RBBr_2$, $RBBr_2{\cdot}SMe_2$, RBI_2, and $RBI_2{\cdot}SMe_2$ derivatives can be carried out according to this procedure. The results obtained with representative dihaloboranes are listed in Table III.

Registry No. 1-Octene, 111-66-0; *cis*-3-octene, 14850-22-7; 1-hexene, 592-41-6; styrene, 100-42-5; 2-methyl-1-pentene, 763-29-1; 2-methyl-2-butene, 513-35-9; 1-methylcyclopentene, 693-89-0; 1-hexanol, 111-27-3; 2-hexanol, 626-93-7; 2-phenylethanol, 60-12-8; 1-phenylethanol, 98-85-1; 2-methyl-1-pentanol, 105-30-6; 2-methyl-2-pentanol, 590-36-3; 3-methyl-2-butanol, 598-75-4; 2-methyl-2-butanol, 75-85-4; *trans*-2-methylcyclopentanol, 25144-04-1; 1-methylcyclopentanol, 1462-03-9; octyldichloroborane, 63348-82-3; octyldichloroborane–dimethyl sulfide, 72205-94-8; *trans*-2-methylcyclopentyldichloroborane–dimethyl sulfide, 72205-95-9; hexyldibromoborane–dimethyl sulfide, 64770-04-3; 3-hexyldibromoborane–dimethyl sulfide, 64770-06-5; 2-methyl-1-pentyldibromoborane–dimethyl sulfide, 72205-97-1; cyclopentyldibromoborane–dimethyl sulfide, 64770-10-1; *trans*-2-methylcyclopentyldibromobrane–dimethyl sulfide, 72205-99-3; hexyldibromoborane, 64770-03-2; octyldiiodoborane–dimethyl sulfide, 72206-01-0; dimethyl hexylboronate, 2344-23-2; dimethyl cyclopentylboronate, 41156-60-9; $HBCl_2{\cdot}SMe_2$, 63462-42-0; $HBBr_2{\cdot}SMe_2$, 55671-55-1; $HBI_2{\cdot}SMe_2$, 55652-51-2.

Hydroboration. 55. Hydroboration of Alkynes with Dibromoborane–Dimethyl Sulfide. Convenient Preparation of Alkenyldibromoboranes

Herbert C. Brown* and James B. Campbell, Jr.[1]

Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907

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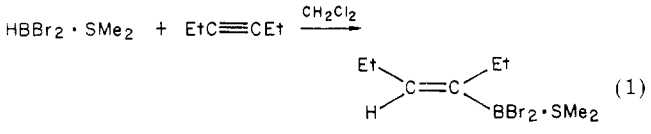
Dibromoborane–dimethyl sulfide undergoes direct hydroboration of both terminal and internal alkynes with remarkable facility to give alkenyldibromoboranes. These reactive alkenylboranes, which may be isolated, undergo many synthetically useful transformations. Oxidation provides the carbonyl compounds while protonolysis with acetic acid occurs stereospecifically to yield the corresponding alkenes. 1-Alkenyldibromoboranes can be converted easily to 1-iodo-1-alkenes by basic hydrolysis and iodination. Both internal and 1-alkenyldibromoboranes serve as convenient precursors to symmetrical conjugated dienes by reaction with 3 equiv of methylcopper. Hydroboration of alkynes with $HBBr_2{\cdot}SMe_2$ is critically examined in terms of relative reactivities of both alkyne and alkene substrates. A very broad reactivity spectrum is evident, with internal acetylenes reacting with remarkable facility. The regiospecificity of the hydroboration of unsymmetrically substituted alkynes indicates $HBBr_2{\cdot}SMe_2$ to be a highly selective reagent, sensitive to both steric and electronic effects. The regioselectivity is compared with that of other hindered hydroborating reagents, such as 9-BBN and disiamylborane.

Dibromoborane–dimethyl sulfide ($HBBr_2{\cdot}SMe_2$) was recently reported to undergo direct reaction with alkenes in refluxing methylene chloride to give alkyldibromoboranes in high yields.[2] The enhanced reactivity of this reagent relative to dichloroborane diethyl etherate ($HBCl_2{\cdot}OEt_2$)[3] and dichloroborane–dimethyl sulfide ($HBCl_2{\cdot}SMe_2$)[4] was somewhat surprising since one might have predicted $HBBr_2{\cdot}SMe_2$, the more stable adduct,[5] to be less reactive than $HBCl_2{\cdot}SMe_2$ for hydroboration. In fact, whereas the dichloroborane adducts require a strong Lewis acid, such as BCl_3, to induce hydroboration, $HBBr_2{\cdot}SMe_2$ reacts directly.[2] The unusual reactivity of $HBBr_2{\cdot}SMe_2$ toward alkenes prompted an investigation of the reaction with alkynes as a possible route to alkenyldibromoboranes. These strongly acidic diheterofunctional alkenylboranes would be anticipated to be fairly reactive intermediates and hence of considerable synthetic interest. Thus, a systematic examination of the hydroboration of alkynes with $HBBr_2{\cdot}SMe_2$ was undertaken as a potential route to the promising alkenyldibromoboranes.

Rate and Stoichiometry. Initially, the rate and stoichiometry of the reaction of $HBBr_2{\cdot}SMe_2$ with 1-hexyne and 3-hexyne, selected as representative terminal and internal alkynes, were investigated. Stoichiometric amounts of the alkyne and $HBBr_2{\cdot}SMe_2$ were employed in CH_2Cl_2 solution at 0 and 25 °C. The reaction rate was followed by monitoring the disappearance of active hydride by hydrolyzing measured aliquots at appropriate intervals of time and determining the volume of the hydrogen evolved. Simultaneously, aliquots were withdrawn, quenched with dilute alkali, and analyzed by gas chromatography for unreacted alkyne. The results, presented in Figure 1 for 3-hexyne, indicate the reaction to be proceeding to form the alkenyldibromoborane (eq 1).



(1)

Likewise, hydroboration of 1-hexyne with $HBBr_2{\cdot}SMe_2$ (Figure 2) appears to form cleanly the corresponding 1-

(1) Graduate research assistant on Grant No. CHE 76-20846 provided by the National Science Foundation.
(2) Brown, H. C.; Ravindran, N. *J. Am. Chem. Soc.* **1977**, *99*, 7097. Brown, H. C.; Ravindran, N.; Kulkarni, S. U. *J. Org. Chem.*, preceding paper in this issue.
(3) Brown, H. C.; Ravindran, N. *J. Am. Chem. Soc.* **1976**, *98*, 1798.
(4) Brown, H. C.; Ravindran, N. *J. Org. Chem.* **1977**, *42*, 2533.
(5) Brown, H. C.; Holmes, R. R. *J. Am. Chem. Soc.* **1956**, *78*, 2173.

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alkenyldibromoborane (eq 2).

$$HBBr_2 \cdot SMe_2 + n\text{-BuC}\equiv\text{CH} \xrightarrow{CH_2Cl_2} \underset{H}{\overset{n\text{-Bu}}{\diagdown}}C{=}C\underset{BBr_2\cdot SMe_2}{\overset{H}{\diagup}} \quad (2)$$

Especially noteworthy are the comparable rates for both hydride and alkyne uptake. This indicates nearly exclusive formation of alkenyldibromoborane with no appreciable complications arising from dihydroboration.[6] Apparently methyl sulfide binds tightly enough to the alkenyldibromoborane produced to provide a large steric factor which inhibits the complex from effectively competing with unreacted alkyne for $HBBr_2 \cdot SMe_2$. Since a 30–40% excess of 1-alkyne is required to suppress significant dihydroboration in the case of monochloroborane etherate ($H_2BCl \cdot OEt_2$),[7] clearly dibromoborane–dimethyl sulfide is a superior reagent to achieve clean monohydroboration of terminal alkynes. Dichloroborane etherate, while undergoing predominantly monohydroboration of 1-alkynes, requires 1 equiv of BCl_3 to induce the reaction.[3] Again, dibromoborane–dimethyl sulfide, which undergoes direct reaction with alkynes, without the need for an added Lewis acid, offers major advantages.

Relative Reactivity of Alkynes and Alkenes toward $HBBr_2 \cdot SMe_2$. The much greater rate at which 3-hexyne is hydroborated by $HBBr_2 \cdot SMe_2$ relative to 1-hexyne elicited considerable interest (compare Figures 1 and 2). Olefins are hydroborated by $HBBr_2 \cdot SMe_2$ readily only in refluxing CH_2Cl_2, while internal alkynes react easily at 0 °C, indicating a large reactivity differential. The possibility of achieving selective hydroboration of internal alkynes in the presence of 1-alkynes and olefins is clearly evident.

In order to examine this selectivity more closely, an investigation was undertaken of the relative reactivities of substrate pairs toward $HBBr_2 \cdot SMe_2$. Typically, 10.0 mmol each of an olefin and/or acetylene were treated with 10.0 mmol of $HBBr_2 \cdot SMe_2$. After proceeding to completion or near completion, the reaction mixture was quenched and analyzed by gas chromatography for the amounts of unreacted substrates. The relative reactivity of the substrate pair was then calculated by the Ingold–Shaw expression (see Experimental Section).[8] The results obtained for several alkynes and alkenes are presented in Table I.

The data indicate a broad spectrum of reactivity between internal alkynes and unactivated internal olefins. The anomalous entry appears to be 3-hexyne, which exhibits an exceptional reactivity toward dibromoborane–dimethyl sulfide, some 20 times greater than that exhibited by 1-hexyne. Qualitatively, the reactivity of all substrates parallels the available π-electron density or π basicity at the unsaturated centers.[9] Undoubtedly, steric factors become more important, with internal olefins balancing out π base effects, as in *cis*-4-octene.

Comparison of the reactivity of $HBBr_2 \cdot SMe_2$, 9-BBN,[10] and bis(3-methyl-2-butyl)borane (Sia_2BH)[11] with various substrates indicates a range of selectivities (Table II). Whereas with 9-BBN, 1-octene can be selectively hydroborated in the presence of either a terminal or an internal alkyne, with $HBBr_2 \cdot SMe_2$, the internal alkyne would react preferentially.[12] Conversely, Sia_2BH would show little selectivity among the three unsaturated substrates.

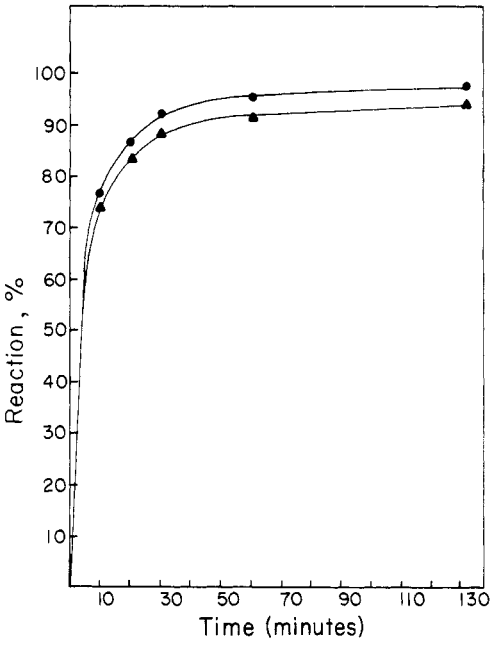


Figure 1. Rates of hydroboration of 3-hexyne at 0 °C: ●, hydride; ▲, alkyne.

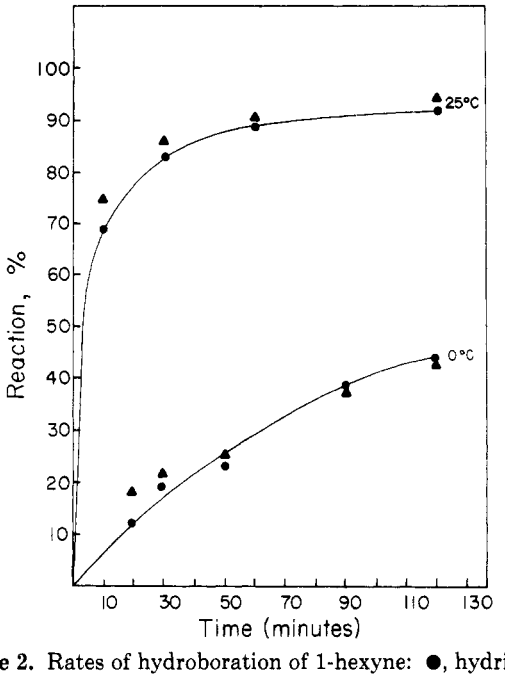


Figure 2. Rates of hydroboration of 1-hexyne: ●, hydride; ▲, alkyne.

Table I. Relative Reactivities of Alkynes and Alkenes toward $HBBr_2 \cdot SMe_2$

alkyne or olefin	rel reactivity[a]	alkyne or olefin	rel reactivity[a]
3-hexyne	5900	phenylacetylene	39
1-hexyne	290	*cis*-4-octene	20
1-octene	100	styrene	6.3
1-phenyl-1-propyne	62	*cis*-propenylbenzene	2.5

[a] Values normalized with 1-octene arbitrarily set to 100.

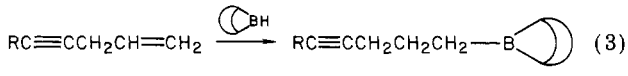
(6) Had appreciable dihydroboration occurred, the rate of hydride uptake would have substantially exceeded the rate of alkyne uptake.
(7) Brown, H. C.; Ravindran, N. *J. Am. Chem. Soc.* **1976**, *98*, 1785.
(8) Ingold, C. K.; Shaw, F. R. *J. Chem. Soc.* **1927**, 2918.
(9) (a) West, R. *J. Am. Chem. Soc.* **1959**, *81*, 1614. (b) Yoshida, Z.; Ishibe, N.; Ozoe, H. *Ibid.* **1972**, *94*, 4948.
(10) Brown, H. C.; Scouten, C. G.; Liotta, R. *J. Am. Chem. Soc.* **1979**, *101*, 96.
(11) Brown, H. C.; Moerikofer, A. W. *J. Am. Chem. Soc.* **1963**, *85*, 2063.
(12) Brown, C. A.; Coleman, R. A. *J. Org. Chem.* **1979**, *44*, 2328.

Table II. Relative Reactivities of Representative Alkynes and Alkenes with Various Hydroborating Reagents

alkyne or olefin	rel reactivity[a]		
	$HBBr_2 \cdot SMe_2$	9-BBN[b]	Sia_2BH[c]
1-octene	100	100	100
cis-3-hexene	20[d]	0.56	1.85
1-hexyne	290	15	345
3-hexyne	5900	0.74	208

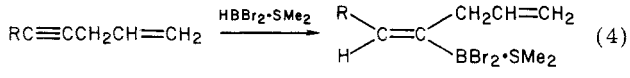
[a] Normalized; 1-octene = 100. [b] Reference 10. [c] Reference 11. [d] *cis*-4-Octene.

An indication of the remarkable selectivities to be anticipated is indicated by the recent selective hydroboration with 9-BBN of representative skipped enynes.[12] The reagent reacts preferentially with the terminal double bond (eq 3).



(3)

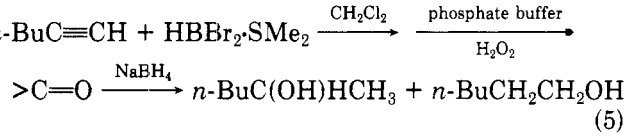
The relative reactivities revealed by the data in Table I predict that $HBBr_2 \cdot SMe_2$ will react selectively at the internal triple bond (eq 4).



(4)

While this selectivity difference provides a much broader synthetic repertoire, there are also interesting theoretical implications. Clearly the steric and electronic factors governing substrate–reagent interactions are quite different among the various hydroborating reagents and merit further investigation.

Regioselectivity of Hydroboration. The directive effect of various unsymmetrically substituted acetylenes toward $HBBr_2 \cdot SMe_2$ was next investigated. Several representative alkynes of varying steric and electronic requirements were chosen. The regiospecificity for the addition of >BH was determined by oxidation of the intermediate alkenyldibromoboranes with alkaline hydrogen peroxide. The distribution of carbonyl isomers was then quantified by GC analysis or by ^1H NMR. In certain cases where the carbonyl isomers could not be easily separated by GC, reduction to the corresponding alcohols by sodium borohydride facilitated separation of the regioisomers and made GC analysis practical. For 1-hexyne, a representative 1-alkyne, oxidation of the intermediate alkenylborane by the standard procedure does not provide a quantitative conversion to the aldehyde. Consequently, 1-hexyne was first hydroborated with $HBBr_2 \cdot SMe_2$ and then oxidized with hydrogen peroxide in the presence of excess phosphate buffer at pH 7. Following reduction of the carbonyls by sodium borohydride, the amount of 2-hexanol detected was used to estimate the directive effect (eq 5).



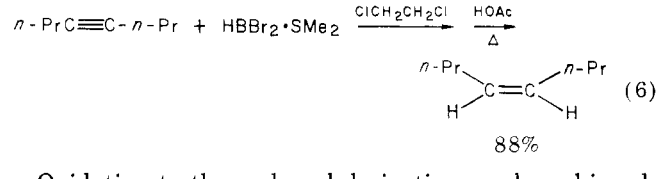
(5)

Since formation of hexenyldibromoborane is essentially quantitative, the remainder of product must arise from placement of boron at the terminal position. The results revealed 2% formation of the secondary isomer, 2-hexanol, indicating 98% formation of the 1-alkenyldibromoborane. Results for a series of 1-substituted propyne derivatives are presented in Table III along with directive effects for several other hydroborating reagents.[13] The results indicate a pronounced directive effect for $HBBr_2 \cdot SMe_2$, placing the boron at the least hindered position. Comparison with 9-BBN reveals very similar behavior for $HBBr_2 \cdot SMe_2$, apparently subject to nearly the same steric and electronic control. Both reagents exhibit amazingly parallel directive effects, even with the large electronic influence of the phenyl substituent in 1-phenyl-1-propyne. Consequently, regiospecific hydroboration with $HBBr_2 \cdot SMe_2$ provides a valuable complement to the selectivity exhibited by 9-BBN.

Isolation of Alkenyldibromoboranes. Isolation of the hydroboration product of alkynes with $HBBr_2 \cdot SMe_2$ by vacuum distillation or recrystallization affords the pure alkenyldibromoboranes as their methyl sulfide addition compounds. The strongly Lewis acidic alkenyldibromoboranes bind tightly enough with methyl sulfide to avoid dissociation, even under vacuum distillation. A few representative isolated alkenyldibromoborane–dimethyl sulfide adducts are given in Table IV. In each case, the isolated boranes were characterized by ^1H NMR, ^{11}B NMR, and, in certain cases, elemental analysis. The purity is estimated to be greater than 98%. In most examples, the alkenyldibromoborane–dimethyl sulfide adducts appeared to be quite sensitive thermally. Although obtained initially by the distillation as colorless liquids, the boranes soon changed, at room temperature, first to orange and then to brown. However, when stored at 0 °C, a temperature at which most were solids, the boranes appeared to be quite stable, undergoing little detectable decomposition after several weeks. All of the alkenyldibromoborane–dimethyl sulfide complexes fume profusely when exposed to air, except in the case of (3,3-dimethyl-1-buten-1-yl)dibromoborane–dimethyl sulfide. This borane proved to be exceptionally stable, even when exposed to moist air for several minutes.

The only examples of such alkenyldibromoboranes reported earlier are ethenyldibromoborane, prepared by reaction of either divinylzinc or divinylmercury with boron tribromide,[14] and several 2-bromo-1-alkenyldibromoboranes, prepared by bromoboration of terminal alkynes with BBr_3.[15] Hence, the direct hydroboration of alkynes with $HBBr_2 \cdot SMe_2$ provides a simple, general, stereospecific route to alkenyldibromoboranes, products not readily available previously.

Reactions of Alkenyldibromoboranes. Alkenyldibromoboranes undergo many of the characteristic reactions of alkenylboranes[16] with or without prior isolation. The presence of dimethyl sulfide does not appear to interfere with any of the reactions examined (vide infra). Protonolysis can be easily achieved by stirring the borane with acetic acid in refluxing ethylene dichloride to give cleanly the corresponding 1-alkenes (from terminal alkynes) or the (*Z*)-alkenes (from internal alkynes) (eq 6).



(6)

88%

Oxidation to the carbonyl derivative can be achieved

(13) Zweifel, G.; Clark, G. M.; Polston, N. L. *J. Am. Chem. Soc.* **1971**, *93*, 3395.
(14) Bartocha, B.; Douglas, C. M.; Gray, M. Y. *Z. Naturforsch.* **1959**, *146*, 809.
(15) (a) Lappert, M. F.; Prokai, B. *J. Organomet. Chem.* **1964**, *1*, 384. (b) Blackborow, J. R. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1989. (c) Blackborow, J. R. *J. Organomet. Chem.* **1977**, *128*, 161.
(16) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975.

Table III. Directive Effects (% Substitution) in 1-Substituted Propynes

$RC^{b}{\equiv}C^{a}CH_3$

hydroborating reagent	R: *n*-Pr b	*n*-Pr a	*i*-Pr b	*i*-Pr a	*t*-Bu b	*t*-Bu a	c-Hx b	c-Hx a	Ph b	Ph a
$HBBr_2{\cdot}SMe_2$	25	75	4	96	0	>99	9	91	64	36
9-BBN[a]	22	78	4	96	0	>99	4	96	65	35
Sia_2BH[b]	39	61	7	93	0	>99	9	91	19	81

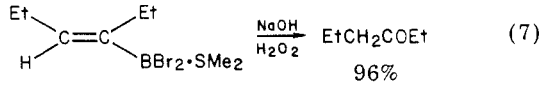
[a] Reference 10. [b] Reference 14.

Table IV. Isolation of Alkenyldibromoborane-Dimethyl Sulfide Adducts

alkyne	product	bp (mmHg) or mp,[a] °C	% yield
1-hexyne	(1*E*)-1-hexen-1-yldibromoborane-dimethyl sulfide	59-60 (0.12)	80
3-hexyne	(3*Z*)-3-hexen-3-yldibromoborane-dimethyl sulfide	53-54 (0.50)	81
3,3-dimethyl-1-butyne	(1*E*)-3,3-dimethyl-1-buten-1-yldibromoborane-dimethyl sulfide	95-96.5	77[b]
4-methyl-2-pentyne	(2*Z*)-4-methyl-2-penten-2-yldibromoborane-dimethyl sulfide	56-58 (0.08)	84
5-chloro-1-pentyne	(1*E*)-5-chloro-1-penten-1-yldibromoborane-dimethyl sulfide	60-62 (0.08)	29[c]

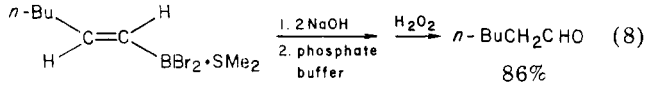
[a] Uncorrected. [b] Yield after recrystallization from $CHCl_3$/hexane. [c] Considerable decomposition occurred during distillation.

with alkaline hydrogen peroxide. However, an additional 2 equiv of base must be added to neutralize the evolved HBr resulting from hydrolysis of the alkenyldibromoboranes. The carbonyl compounds are obtained in excellent yields (eq 7). No especial precaution is required



(7)

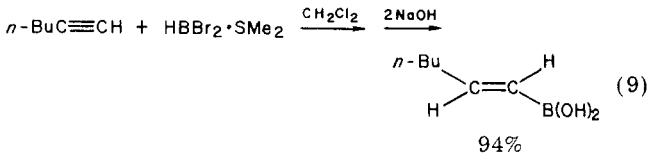
for the boranes from internal alkynes. For 1-alkenyldibromoboranes, the sensitivity of the aldehyde to alkali requires a modified procedure. In this case, the oxidation requires careful initial neutralization of the hydrobromic acid with 2 equiv of base, followed by addition of excess phosphate buffer to maintain the pH close to 7. The oxidation is then carried out by the dropwise addition of hydrogen peroxide (eq 8).



(8)

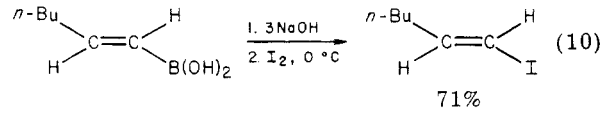
The reaction of 1-alkenylboronic acid with iodine in the presence of base has been demonstrated to provide stereospecifically the corresponding 1-iodo-1-alkenes.[17] Conceivably, basic hydrolysis of 1-alkenyldibromoboranes should afford the requisite alkenylboronic acids which could be isolated and converted into the stereodefined 1-iodo-1-alkene. Alternatively, the 1-alkenyldibromoborane could be hydrolyzed to the boronic acid, and the latter utilized in situ, without isolation.

To test the possibilities, we hydroborated 1-hexyne with $HBBr_2{\cdot}SMe_2$, followed by hydrolysis with 2 equiv of aqueous sodium hydroxide. The desired 1-hexenylboronic acid was obtained in 94% yield after recrystallization from water (eq 9). The isolated boronic acid was then converted



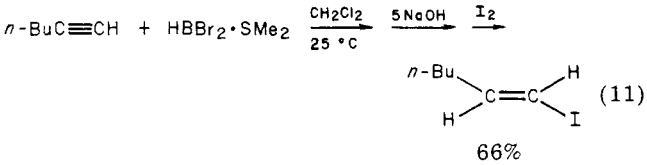
(9)

to *trans*-1-iodo-1-hexene in 71% yield by successive treatment with 3 equiv of sodium hydroxide and 1 equiv of iodine at 0 °C (eq 10).



(10)

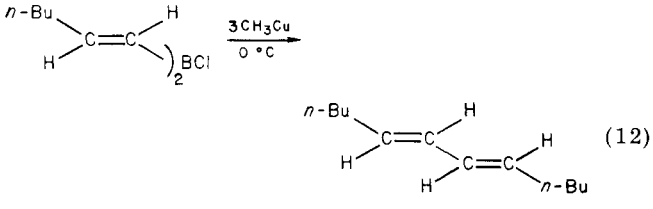
The reaction was then carried out without isolation of the intermediate. The alkyne, 1-hexyne, was first hydroborated, then hydrolyzed by the addition of 5 equiv of aqueous alkali to yield the boronic acid (or salt), and finally treated with iodine to form the alkenyl iodide (eq 11). The



(11)

yield proved to be quite comparable to that realized with the isolated, purified boronic acid. Hence, stereodefined 1-alkenyl iodides can be conveniently prepared by this one-pot procedure without isolation of the intermediate.

Recently, dialkenylchloroboranes have been converted to (*E,E*)-1,3-dienes in excellent yield and high stereochemical purity by treatment with 3 equiv of methylcopper (eq 12).[18] The reaction presumably proceeds via an initial



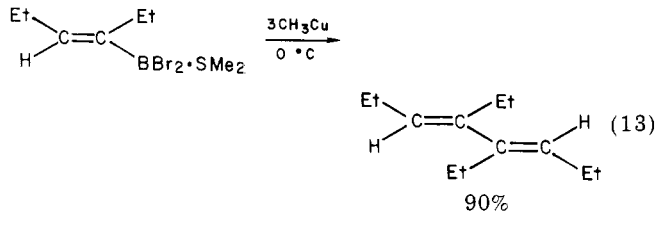
(12)

displacement of chloride by 1 equiv of methylcopper, followed by formation of a dimethyldialkenylborate complex with a second equivalent. The cuprous dimethyldialkenylborate is then postulated to undergo dissociation to afford an alkenylcopper intermediate, which next undergoes thermally induced dimerization to yield the diene.[19]

(17) Brown, H. C.; Hamaoka, T.; Ravindran, N. *J. Am. Chem. Soc.* **1973**, *95*, 5786.

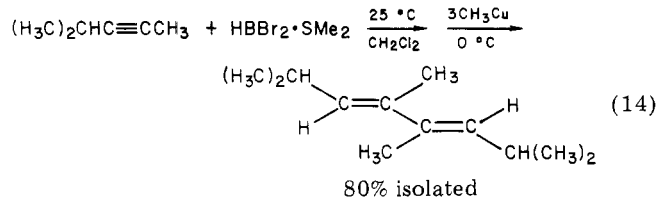
(18) Yamamoto, Y.; Yatagai, H.; Sonoda, A.; Murahashi, S. I.; Moritani, I. *J. Am. Chem. Soc.* **1977**, *99*, 5652.

On the basis of the proposed methanism, alkenyldibromoboranes could also serve as suitable precursors for the synthesis of the desired alkenylcopper reagents and the 1,3-dienes. Accordingly, isolated *cis*-3-hexenyldibromoborane–dimethyl sulfide was treated with 3 equiv of CH_3Cu at 0 °C (eq 13). An excellent yield of the desired



(13)

diene was obtained. The reaction can be performed without prior isolation of the borane, providing a major advantage over the corresponding application of the dialkenylchloroboranes (eq 14).



(14)

As mentioned previously, an excess of 1-alkyne is required for clean monohydroboration with $H_2BCl{\cdot}OEt_2$, whereas $HBBr_2{\cdot}SMe_2$ requires only stoichiometric quantities of the reagents. Hence, use of alkenyldibromoboranes as precursors to the alkenylcopper reagents and to 1,3-dienes appears highly promising.

Conclusion

Dibromoborane–dimethyl sulfide cleanly undergoes monohydroboration of alkynes to afford alkenyldibromoboranes as their methyl sulfide adducts. The unusually facile rate of hydroboration of internal acetylenes relative to terminal acetylenes and olefins allows selective hydroboration. The regiospecificity of hydroboration is also remarkably selective, approaching that of 9-BBN, a highly selective reagent. Finally, the high reactivity of alkenyldibromoboranes renders them exceptionally useful as synthetic intermediates. Undoubtedly, their chemistry will prove to be rich, both synthetically and theoretically.

Experimental Section

General Methods. All glassware was predried at 140 °C for at least 4 h, assembled hot, and cooled under a stream of prepurified dry nitrogen (Airco). All transformations of boron reagents were conducted under a nitrogen atmosphere by using extensively the techniques outlined in Chapter 9 of ref 16. Dibromoborane–dimethyl sulfide was prepared from BBr_3 (Alfa/Ventron) and borane–dimethyl sulfide (Aldrich), as described previously.[20] Alkynes used were commercial samples, which were distilled under nitrogen from a small amount of $NaBH_4$ and stored at 0 °C. The olefins were also all commercially available and were distilled from $LiAlH_4$ before use. CH_2Cl_2 was pretreated by stirring over concentrated H_2SO_4 and distilling from P_2O_5. Methyllithium (Alfa/Ventron) was standardized by the Watson–Eastham titration.[21] ^1H NMR spectra (δ, relative to Me_4Si) were recorded on a Varian T-60 spectrometer. Both ^{13}C (δ, relative to Me_4Si) and ^{11}B (δ, relative to $BF_3{\cdot}OEt_2$) NMR spectra were recorded on a Varian FT-80A spectrometer equipped with a broad-band probe and a Hewlett-Packard 3335A frequency synthesizer. IR spectra were taken on a Perkin-Elmer 700 spectrometer. Elemental analyses were performed by the Departmental Microanalytical Laboratory.

Standardization and Characterization of $HBBr_2{\cdot}SMe_2$. Neat $HBBr_2{\cdot}SMe_2$ is a low-melting solid (mp 30–33 °C) exhibiting a single ^{11}B NMR resonance at δ −7.6 and a sharp ^1H NMR singlet (SCH_3) at δ 2.47, both in CH_2Cl_2. The material was standardized by hydrolyzing measured aliquots and determining the volume of evolved H_2 or titrating the liberated HBr with standard NaOH solution to a methyl orange end point. The amount of boron present, reflected in the amount of boric acid obtained after hydrolysis, was determined by adding excess mannitol to a sample already titrated to a methyl orange end point and continuing to titrate with base to a phenolphthalein end point. The standard error for hydride, bromide, and boron determination proved to be less than 3%. One sample analyzed as described above gave the following results: [hydride] = 7.70 M; [HBr] = 15.72 M; $[B(OH)_3]$ = 7.83 M.

Rate of Hydroboration of Alkynes with $HBBr_2{\cdot}SMe_2$. The following procedure for 1-hexyne is representative. To a 50-mL flask was added 1.14 mL (0.822 g, 10.0 mmol) of 1-hexyne, 0.81 mL (5.0 mmol) of *n*-octane, and 5.0 mL of CH_2Cl_2. To the rapidly stirring solution maintained at 25 °C was added 1.29 mL (10.0 mmol) of $HBBr_2{\cdot}SMe_2$ dissolved in 1.80 mL of CH_2Cl_2 over a period of 4–5 min. The concentration of $HBBr_2{\cdot}SMe_2$ was 1.0 M. At selected time intervals, aliquots were removed and either hydrolyzed in excess aqueous NaOH at 0 °C or hydrolyzed in $MeOH/H_2O$/glycerol (1:1:1), and the volume of evolved hydrogen was measured. The amount of unreacted alkyne was determined by GC analysis on a 10% SE-30 column (6 ft × $^1/_4$ in.; on Chromosorb W) vs. the *n*-octane standard. The volume of collected hydrogen measured at selected intervals was corrected for water vapor pressure, aliquot volume displacement, and atmospheric pressure to calculate the millimoles of active hydride. The simultaneous determination of both active hydride and unreacted alkyne allowed not only monitoring of the reaction rate but also the extent of dihydroboration.[6]

Relative Reactivity of Alkene/Alkyne Pairs toward $HBBr_2{\cdot}SMe_2$. A typical experimental procedure for determining the relative reactivities of 1-phenyl-1-propyne vs. 1-octene follows. To a 50-mL flask was added 5.0 mL of CH_2Cl_2, 0.89 mL (0.628 g, 4.89 mmol) of *n*-nonane (VPC internal standard), 1.24 mL (1.187 g, 10.2 mmol) of 1-phenyl-1-propyne, and 1.57 mL (1.120 g, 10.0 mmol) of 1-octene. Neat $HBBr_2{\cdot}SMe_2$ (1.29 mL, 10.0 mmol) was added slowly to the rapidly stirring reaction mixture, with the temperature being maintained at 25 °C. The reaction was stirred 4 h at 25 °C followed by cooling to 0 °C and quenching with excess 3 N NaOH (7.5 mL). After the mixture was warmed to room temperature and stirred for 30 min, the aqueous layer was saturated with NaCl after the CH_2Cl_2 layer had been separated. After being dried over anhydrous K_2CO_3, the organic layer was analyzed by GC analysis on a 10% SE-30 column (6 ft × $^1/_4$ in.; on Chromosorb W; for boranes only). There was found 6.06 mmol of 1-phenyl-1-propyne and 4.33 mmol of 1-octene. The relative reactivity of this substrate pair as well as other substrate pairs was calculated by the Ingold–Shaw equation (eq 15),[7]

$$\text{relative rate} = \frac{k_X}{k_Y} = \frac{\log X_0 - \log X_{00}}{\log Y_0 - \log Y_{00}}$$

where X_0 = initial concentration of X and X_{00} = final concentration of X, etc. For the representative example of 1-phenyl-1-propyne and 1-octene, $k_{1\text{-octene}}/k_{1\text{-phenyl-1-propyne}} = 1.60$.

Regioselectivity of Hydroboration of Unsymmetrically Substituted Alkynes with $HBBr_2{\cdot}SMe_2$. The regioselectivity of hydroboration was determined by oxidizing the intermediate alkenylboranes to the corresponding carbonyl compounds with basic hydrogen peroxide.

(i) By ^1H NMR Analysis. To a 25 °C solution containing 0.62 mL (0.575 g, 4.95 mmol) of 1-phenyl-1-propyne and 0.26 mL (0.329 g, 3.87 mmol) of CH_2Cl_2 in 2.0 mL of $CDCl_3$ was added 0.66 mL (5.0 mmol) of $HBBr_2{\cdot}SMe_2$. After being stirred for 3 h at room temperature, the reaction was cooled to 0 °C and quenched by

(19) Whitesides, G. M.; Casey, C. P.; Krieger, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 1379.
(20) Brown, H. C.; Ravindran, N. *Inorg. Chem.* **1977**, *16*, 2938. The rate of redistribution appears to vary with individual samples of borane–dimethyl sulfide. This phenomenon is under investigation.
(21) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

adding 5.0 mL of 3 N NaOH. After warming to room temperature and equilibrating, the mixture was oxidized by the dropwise addition of 2.5 mL of 30% H_2O_2. The reaction was stirred at 25 °C for 6 h to ensure complete oxidation. The aqueous layer was saturated with K_2CO_3 and the organic layer separated. After being dried over anhydrous Na_2SO_4, the clear organic layer was analyzed by ^1H NMR. The benzylic protons of phenylacetone (δ 3.67) were integrated against the methyl triplet of propiophenone vs. the CH_2Cl_2 internal standard. After normalization of the number of protons contributing to each resonance, there was found 1.74 mmol (35%) of phenylacetone and 3.01 mmol (61%) of propiophenone. Hence, 64% of the boron had been placed α to the phenyl group of 1-phenyl-1-propyne with 36% β to the phenyl.

(ii) By Gas Chromatographic Analysis. To a 25 °C solution of 0.62 mL of 1-phenyl-1-propyne (0.581 g, 5.00 mmol) and 0.80 mL of *n*-undecane (0.605 g, 3.87 mmol) in 2.0 mL of CH_2Cl_2 was added 0.64 mL (5.0 mmol) of $HBBr_2{\cdot}SMe_2$ dissolved in 3.3 mL of CH_2Cl_2. After 3 h at 25 °C, the reaction was cooled to 0 °C, quenched with 5 mL of 3 N NaOH, and oxidized by adding 2.5 mL of 30% H_2O_2. The aqueous layer was saturated with K_2CO_3 and the organic layer separated. Ethanol was added (2.0 mL), followed by excess $NaBH_4$. After the mixture was stirred at 25 °C for 5 h, the excess $NaBH_4$ was quenched with dilute HCl and the aqueous layer saturated with NaCl. After this mixture was dried over K_2CO_3 and analyzed by GC on a 10% Carbowax 20M (on Chromosorb W; 6 ft × $^1/_4$ in.) column, there was obtained 2.88 mmol (58%) of 1-phenyl-1-propanol and 1.63 mmol (33%) of 1-phenyl-2-propanol. This corresponds to a regioselectivity identical with that obtained above by ^1H NMR analysis.

Isolation and Characterization of Alkenyldibromoborane–Dimethyl Sulfide Complexes. The procedure for isolation of (a) (3*Z*)-3-hexen-3-yldibromoborane–dimethyl sulfide is representative. To a solution of 4.19 g (51.0 mmol) of 3-hexyne in 15 mL of CH_2Cl_2 maintained at 10–15 °C was added dropwise a solution containing 6.41 mL (50.0 mmol) of $HBBr_2{\cdot}SMe_2$ in 10 mL of CH_2Cl_2. After completion of the addition of the $HBBr_2{\cdot}SMe_2$ solution, the cold bath was removed, and the reaction was warmed to room temperature and then stirred for 1 h. The solvent was removed by using aspirator vacuum and the crude borane distilled at 53–54 °C (0.50 mmHg) to give 12.8 g (40.5 mmol, 81%) of a clear oil. The product, which melted at 5–8 °C, was estimated to be >98% pure by NMR analysis: ^1H NMR ($CDCl_3$) δ 6.10 (t, 1 H, J = 7 Hz), 2.38 (s, 6 H, SCH_3), 2.2–2.4 (m, 4 H), 1.03 (t, 3 H, J = 7 Hz), 1.00 (t, 3 H, J = 7 Hz). ^{11}B NMR ($CDCl_3$) δ −3.3.

Anal. Calcd for $C_8H_{17}Br_2BS$: C, 30.41; H, 5.42; Br, 50.59; S, 10.15; B, 3.42. Found: C, 30.55; H, 5.34; Br, 50.11; S, 9.89; B, 3.46.

Oxidation of the isolated alkenylborane provided a 97% yield of 3-hexanone.

For preparation of the 1-alkenyldibromoboranes, the hydroboration requires 4–5 h of stirring at 25 °C for completion. Other alkenyldibromoborane–dimethyl sulfide adducts isolated are as follows.

(b) (1*E*)-1-Hexen-1-yldibromoborane–dimethyl sulfide: bp 59–60 °C (0.12 mmHg); 12.64 g, 80% yield; ^1H NMR ($CDCl_3$) δ 6.08 (dt, 1 H, J = 6, 16.8 Hz), 5.62 (d, 1 H, J = 16.8 Hz), 2.38 (s, 6 H, SCH_3), 2.3 (m, 2 H), 1.40 (m, 4 H), 0.90 (t, 3 H, J = 6 Hz); ^{11}B NMR (CCl_4) δ −0.92. Buffered oxidation revealed an 84% yield of *n*-hexanal (GC).

(c) (1*E*)-3,3-Dimethyl-1-buten-1-yldibromoborane–dimethyl sulfide: mp (uncor) 95–96.5 °C (recrystallized from $CHCl_3$/hexane); 12.11 g, 77% yield; ^1H NMR ($CDCl_3$) δ 6.28 (d, 1 H, J = 17 Hz), 5.51 (d, 1 H, J = 17 Hz), 2.37 (s, 6 H, SCH_3), 1.03 (s, 9 H); ^{11}B NMR (CCl_4) δ 0.3.

Anal. Calcd for $C_8H_{17}Br_2BS$: C, 30.41; H, 5.42; Br, 50.59; S, 10.15; B, 3.42. Found: C, 30.43; H, 5.35; Br, 50.44; S, 10.21; B, 3.46.

Buffered oxidation gave a 77% yield of 3,3-dimethylbutanal (^1H NMR analysis).

(d) (2*Z*)-4-Methyl-2-penten-2-yldibromoborane–dimethyl sulfide: bp 56–58 °C (0.08 mmHg); 13.31 g, 84% yield; mp (uncor) 57–58 °C; ^1H NMR ($CDCl_3$) δ 5.85 (d, 1 H, J = 9 Hz), 2.6 (m, 1 H), 2.35 (s, 6 H, SCH_3), 1.73 (d, 3 H, J = 1 Hz), 0.97 (d, 6 H, J = 6 Hz); ^{11}B NMR (CCl_4) δ −3.6. Oxidation with basic H_2O_2 provided a 99% yield (GC) of 4-methyl-2-pentanone.

(e) (1*E*)-5-Chloro-1-penten-1-yldibromoborane–dimethyl sulfide: bp 60–62 °C (0.08 mmHg) (substantial decomposition occurred during distillation); 4.87 g, 29% yield; ^1H NMR ($CDCl_3$) δ 6.13 (dt, 1 H, J = 6, 17 Hz), 5.62 (d, 1 H, J = 17 Hz), 3.52 (t, 2 H, J = 6 Hz), 2.43 (s, 6 H, SCH_3), 2.18 (m, 4 H); ^{11}B NMR (CCl_4) δ −2.0.

Protonolysis of Alkenyldibromoborane–Dimethyl Sulfide Adducts. To a 50-mL flask equipped with a reflux condenser was added 1.47 mL (1.107 g, 10.0 mmol) of 4-octyne, 1.43 mL (1.027 g, 8.01 mmol) of *n*-nonane, and 10.0 mL of 1,2-dichloroethane. The solution was cooled to 10–15 °C by a cold-water bath and 1.28 mL (10.0 mmol) of neat $HBBr_2{\cdot}SMe_2$ slowly added. After the complete addition of $HBBr_2{\cdot}SMe_2$, the reaction was stirred for 15 min at 10–15 °C, followed by 30 min at room temperature. Glacial acetic acid (2.5 mL, 45 mmol) was added and the reaction mixture heated to gentle reflux for 3 h. After the mixture was cooled to 0 °C and neutralized with 3 N NaOH, a small aliquot was removed, dried over K_2CO_3, and analyzed by GC. There was found 8.82 mmol of *cis*-4-octene, a yield of 88%.

Preparation of (1*E*)-1-Hexenylboronic Acid. To a solution of 1-hexyne (12.6 mL, 110 mmol) in 40 mL of CH_2Cl_2, cooled to 10–15 °C, was added dropwise a solution of 12.8 mL (100 mmol) of $HBBr_2{\cdot}SMe_2$ in 15 mL of CH_2Cl_2. The reaction mixture was stirred for 4 h following the addition of the $HBBr_2{\cdot}SMe_2$. The volatile components were removed under protected water aspirator vacuum, and the crude 1-hexenyldibromoborane was dripped via a double-ended needle into a solution of 220 mmol of NaOH maintained at 0 °C. Following the addition, the mixture was stirred for 2 h at room temperature. An additional 50 mL of H_2O was then added and the precipitated boronic acid collected. After being cooled to 0 °C and washed with ice-cold H_2O, the crystals were collected and dried in an evacuated desiccator overnight. There was obtained 12.1 g or 94% of 1-hexenylboronic acid.

Conversion of (1*E*)-1-Hexenylboronic Acid to (1*E*)-1-Iodo-1-hexene. 1-Hexenylboronic acid (88 mmol, 11.3 g) was dissolved in 90 mL of diethyl ether and cooled to 0 °C. To this was added 88 mL (264 mmol) of 3 N NaOH. A solution of 26.6 g (105 mmol) of I_2 in 300 mL of ether was added over a period of 30 min with vigorous stirring. After the complete addition, the reaction was stirred for 30 min at 0 °C, followed by the addition of a few drops of saturated aqueous $Na_2S_2O_3$ solution to remove residual iodine. After the mixture had been stirred for an additional 30 min, the ether layer was separated and the aqueous layer extracted with ether (3 × 30 mL). The combined ether layer was dried over anhydrous $MgSO_4$, followed by removal of the volatile components and distillation under reduced pressure; bp 44–45 °C (2.4 mmHg). There was obtained 13.1 g (62.4 mmol) or 71% of a light orange liquid. The product was >98% pure by GC and ^1H NMR. The overall yield from $HBBr_2{\cdot}SMe_2$ was 67%: ^1H NMR ($CDCl_3$) δ 6.50 (dt, 1 H, J = 6.5, 14 Hz), 5.94 (d, 1 H, J = 14 Hz), 2.04 (m, 2 H), 1.39 (m, 4 H), 0.90 (t, 3 H, J = 6 Hz); n^{20}_D 1.5084 (lit.[21] n 1.5072); IR (max, neat) 1600, 960 cm^{-1}.

Direct One-Pot Conversion of 1-Hexyne to (1*E*)-1-Iodo-1-hexene. 1-Hexyne (90.0 mmol, 7.40 g) was taken up in 20.0 mL of CH_2Cl_2 and cooled to 0–5 °C. To this was added dropwise 11.5 mL (90.0 mmol) of $HBBr_2{\cdot}SMe_2$ dissolved in 10 mL of CH_2Cl_2. After the addition was complete, the cold bath was removed, and the reaction was warmed to 25 °C and stirred for 4 h. The volatiles were removed under aspirator vacuum, and the crude borane was decanted with rapid stirring into 150 mL of 3 N NaOH (5 equiv) cooled to 0 °C. After the mixture had been stirred for 30 min at 0 °C, 50 mL of ether was added, followed by the dropwise addition of 25.4 g (100 mmol) of I_2 dissolved in 270 mL of ether. Following the complete addition of the I_2, the reaction was stirred at 0 °C for 30 min, followed by warming to 25 °C and stirring for an additional 30 min. Excess I_2 was then destroyed with a few drops of saturated $Na_2S_2O_3$ solution. The ether layer was separated and the aqueous phase extracted with ether (3 × 30 mL). The combined organic phase was dried over anhydrous $MgSO_4$, followed by removal of the ether under aspirator vacuum and distillation of the crude product. There was obtained 11.9 g (57 mmol, 64%) of the alkenyl iodide. The purified material was identical with an authentic sample in all physical and spectroscopic properties: bp 44–45 °C (2.5 mmHg); n^{20}_D 1.5077.

Preparation of (*E*,*E*)-1,3-Dienes via Methylcopper-Induced Coupling of Alkenyldibromoboranes. The preparation

and isolation of (3*E*,5*E*)-2,4,5,7-tetramethyl-3,5-octadiene[22] serves as a representative example. A suspension of methylcopper in ether was prepared by the dropwise addition of 54.5 mL (81 mmol) of CH_3Li to a 0 °C suspension of 15.45 g (81 mmol) of CuI in 15 mL of ether. The resultant yellow slurry was stirred for 15 min at 0 °C to ensure complete conversion to CH_3Cu. A solution of 4-methyl-2-penten-2-yldibromoborane–dimethyl sulfide (8.25 g, 26.1 mmol) dissolved in 10 mL of ether was added to the CH_3Cu slurry. The reaction mixture was stirred at 0 °C for 45 min, followed by warming to room temperature and then stirring for an additional 30 min. After the mixture was again cooled to 0 °C, excess saturated NH_4Cl solution was added and the reaction warmed to 25 °C. The organic layer was separated and the copper residue washed with ether (3 × 20 mL). The combined organic layer was dried over anhydrous $MgSO_4$ followed by removal of the volatiles under aspirator vacuum. Kugelrohr distillation at reduced pressure afforded 1.72 g (10.4 mmol, 80%) of a clear liquid. The product was >95% pure by GC: oven distillation temperature 55–60 °C (3.0 mmHg); n^{20}_D 1.4662; ^{1}H NMR ($CDCl_3$) δ 5.30 (d, 2 H, *J* = 8 Hz), 2.55 (m, 2 H), 1.75 (d, 6 H, *J* = 1 Hz), 0.93 (d, 12 H, *J* = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 134.01, 133.38, 27.62, 23.08, 13.85; IR 3.43, 3.48, 6.85, 7.30, 10.2, 12.0 μm.

(22) Zweifel, G.; Whitney, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 2753.

Registry No. 3-Hexyne, 928-49-4; 1-hexyne, 693-02-7; 1-octene, 111-66-0; 1-phenyl-1-propyne, 673-32-5; phenylacetylene, 536-74-3; *cis*-4-octene, 7642-15-1; styrene, 100-42-5; *cis*-propenylbenzene, 766-90-5; *cis*-3-hexene, 7642-09-3; 2-hexyne, 764-35-2; 4-methyl-2-pentyne, 21020-27-9; 4,4-dimethyl-2-pentyne, 999-78-0; 1-propynylcyclohexane, 18736-95-3; 3,3-dimethyl-1-butyne, 917-92-0; 5-chloro-1-pentyne, 14267-92-6; (*E*)-1-hexen-1-yldibromoborane–dimethyl sulfide, 72228-56-9; (*Z*)-3-hexen-3-yldibromoborane–dimethyl sulfide, 72228-58-1; (*E*)-3,3-dimethyl-1-buten-1-yldibromoborane–dimethyl sulfide, 72228-60-5; (*Z*)-4-methyl-2-penten-2-yldibromoborane–dimethyl sulfide, 72228-62-7; (*E*)-5-chloro-1-penten-1-yldibromoborane–dimethyl sulfide, 72228-64-9; $HBBr_2{\cdot}SMe_2$, 55671-55-1; phenylacetone, 103-79-7; propiophenone, 93-55-0; 1-phenyl-1-propanol, 93-54-9; 1-phenyl-2-propanol, 698-87-3; 3-hexanone, 589-38-8; hexanal, 66-25-1; 3,3-dimethylbutanal, 2987-16-8; 4-methyl-2-pentanone, 108-10-1; 4-octyne, 1942-45-6; (*E*)-1-hexenylboronic acid, 42599-18-8; (*E*)-1-hexenyldibromoborane, 72228-55-8; (*E*)-1-iodo-1-hexene, 16644-98-7; (*E*,*E*)-2,4,5,7-tetramethyl-3,5-octadiene, 63787-85-9; methylcopper, 1184-53-8; (*E*,*E*)-4,5-diethyl-3,5-octadiene, 72228-65-0.

Three-Carbon Annelations. Regiocontrolled Reactivity of Trimethylsilyl- and Ethoxyethyl-Protected Cyanohydrins. Versatile Homoenolate and Acyl Anion Equivalents

Richard M. Jacobson,* George P. Lahm, and John W. Clader

Department of Chemistry, Indiana University, Bloomington, Indiana 47405

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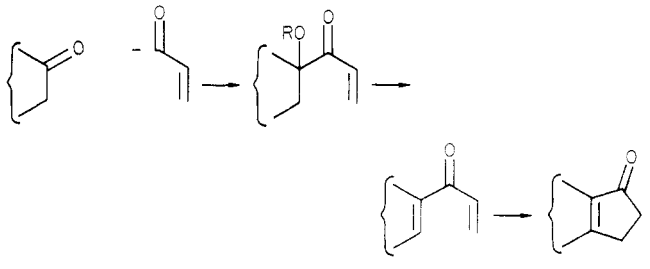
The trimethylsilyl- (**2**) and ethoxyethyl- (**4**) protected cyanohydrins of α,β-unsaturated aldehydes are utilized as three-carbon annelation reagents. Metalated reagent **2** displays exclusive α reactivity with aldehydes and ketones at −78 °C. Metalated reagent **4** displays exclusive α reactivity at −78 °C and exclusive γ reactivity at 0 °C. Reagent **4** thus allows for complete regiocontrol in its addition to aldehydes and ketones which permits selective addition of either a homoenolate or an acyl anion equivalent. Metalation of the α product **11** at −78 °C with subsequent warming to 0 °C produces exclusively the γ product, confirming the reversible nature of the addition to the carbonyl. The derived α′-trimethylsiloxy enones **17** (R_3 = Me_3Si), α′-hydroxy enones **17** (R_3 = H), α′-acetoxy enones **17** (R_3 = Ac), and γ-lactones **10** are useful cyclopentenone precursors. Treatment of **17** with *p*-TsOH in toluene at reflux produces cyclopentenones. The reaction proceeds via the postulated intermediacy of a pentadienyl cation **15** which undergoes in situ electrocyclic ring closure.

As cyclopentyl ring systems are found in a wide variety of natural products, methods which allow for their construction have been a topic of current discussion.[1] We have been especially interested in annelative techniques for cyclopentane construction. The widely used Robinson annelation has no such general counterpart in the synthesis of cyclopentane ring systems. Although a variety of useful three-carbon annelation techniques exist there is a continuing need for the development of new methodology.

We felt that the electrocyclic ring closure of 1,4-pentadien-3-ones (Nazarov cyclization)[2] would prove useful if a facile method for their preparation were available.[3] Retrosynthetic analysis prompted us to consider the addition of acyl anion equivalents of α,β-unsaturated aldehydes to carbonyl compounds. Dehydration of the addition product would generate the pentadienone system we desired.



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