

Directive Effects in the Monohydroboration of Alkynes and Enynes¹

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Abstract: Monohydroboration of terminal alkynes such as 1-octyne and phenylacetylene with dicyclohexylborane or thexylborane (2,3-dimethyl-2-butylborane) places the boron nearly exclusively at the terminal position of the triple bond. 2-Methyl-1-buten-3-yne and 1-ethynylcyclohexene react similarly with these mono- and dialkylboranes to afford high yields of the corresponding terminal dienylboranes. The direction of addition of dicyclohexylborane or disiamylborane (bis(3-methyl-2-butyl)borane) to unsymmetrically disubstituted alkynes is markedly affected by the size of the substituents attached to the triple bond. Thus, the *tert*-butyl group directs the boron nearly exclusively to the less hindered position of the triple bond of *tert*-butylmethylacetylene, *tert*-butyl-*n*-butylacetylene, and *tert*-butylisopropylacetylene. Also, secondary alkyl groups direct the boron at least 85% toward the *n*-alkyl-substituted end of a triple bond. This observed regioselectivity in the hydroboration of disubstituted alkynes thus provides a convenient route for the selective synthesis of highly substituted ketones *via* the hydroboration-oxidation reaction. Thexylborane displays a high selectivity for the less hindered carbon of the triple bond in *tert*-butyl-*n*-alkylacetylenes. However, replacing the *tert*-butyl by a *sec*-alkyl group results in significant loss of selectivity for the attack at the carbon carrying the *n*-alkyl substituent. Finally, borane is essentially nonselective in its addition to disubstituted alkynes.

The hydroboration of olefins provides a convenient route to organoboranes³ and, *via* further reactions of these, to a variety of functionally substituted alkenes.⁴ Numerous reports have appeared in which the addition of borane or dialkylboranes to olefins has been shown to possess high regioselectivity. On the other hand, relatively few investigations concerning the regioselectivity of addition of borane or alkylboranes to alkynes have been reported.

Symmetrical disubstituted alkynes, such as 3-hexyne, may be converted into vinylboranes by using either borane or disiamylborane. However, attempts to convert 1-alkynes into vinylboranes using borane as the hydroborating agent resulted in the formation of dihydroborated products, in which both boron atoms are predominantly attached at the terminal carbon of the triple bond.^{5,6} On the other hand, hydroboration of terminal acetylenes with the more hindered reagents disiamylborane⁵ and thexylborane⁷ provides a satisfactory route to the vinylboranes. Oxidation with alkaline hydrogen peroxide produces the corresponding aldehydes in better than 80% yields,^{5,7} pointing to a preferential attack of the boron at the less hindered terminal position of the triple bond.

Investigations of the utilization of vinylboranes as intermediates in organic syntheses have opened many new routes for the derivatization of triple bonds. Thus, alkynes have been converted into aldehydes,⁵ ketones,⁵ and olefins,³ 1-halo-1-alkenes,⁸ *cis*-disubstituted olefins,⁹

and *cis,trans*-1,3-dienes¹⁰ *via* the intermediate vinylboranes. Moreover, since the hydroboration reaction accommodates many functional groups,³ 1-halo-1-alkynes,¹¹ propargyl chlorides,¹² and α,β -acetylenic esters¹³ are also readily transformed into the corresponding vinylboranes.

Surprisingly, no study of the direction of addition of alkylboranes to unsymmetrically disubstituted alkynes has been reported. Because of the well-documented selectivity of various dialkylboranes in the hydroboration of unsymmetrically disubstituted olefins,³ it was anticipated that monohydroboration of analogous alkynes with alkylboranes should also result predominantly in the addition of boron at the less hindered positions of the triple bonds. Thus, a variety of disubstituted vinylboranes of predictable structure could be prepared.

In view of the important synthetic potentialities of vinylboranes, it was felt that a detailed investigation of their preparation was warranted. Hence, a study of the direction of addition of borane and its thexyl, dicyclohexyl, and disiamyl derivatives to representative terminal alkynes, enynes, and unsymmetrically disubstituted alkynes was carried out and is reported in this paper.

Results and Discussion

Monohydroboration of Terminal Acetylenes. It was shown previously that monohydroboration of 1-hexyne with disiamylborane⁵ or thexylborane⁷ yielded, after oxidation, 88 and 82%, respectively, *n*-hexaldehyde. Thus, the preferential addition of boron to the terminal carbon of the triple bond was indicated. In order to establish more definitely the regioselectivity and stereoselectivity of the monoaddition of alkylboranes to 1-alkynes, 1-octyne and phenylacetylene have now been hydroborated with dicyclohexylborane and thexylborane. To achieve a more quantitative measure (inde-

(1) This research was supported by the National Science Foundation through Grant No. GP-9398.

(2) National Defense Education Act Fellow (Title IV) at the University of California, Davis, 1968-1970.

(3a) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962; (b) G. Zweifel and H. C. Brown, *Org. React.*, **13**, 1 (1963).

(4) H. C. Brown, *Accounts Chem. Res.*, **2**, 65 (1969).

(5) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **83**, 3834 (1961).

(6) For a detailed study concerning the dihydroboration of 1-hexyne, see G. Zweifel and H. Arzoumanian, *ibid.*, **89**, 291 (1967).

(7) G. Zweifel and H. C. Brown, *ibid.*, **85**, 2066 (1963).

(8) H. C. Brown, D. H. Bowman, S. Misumi, and M. K. Unni, *ibid.*, **89**, 4531 (1967).

(9) G. Zweifel, H. Arzoumanian, and C. C. Whitney, *ibid.*, **89**, 3652 (1967).

(10) G. Zweifel, N. L. Polston, and C. C. Whitney, *ibid.*, **90**, 6243 (1968).

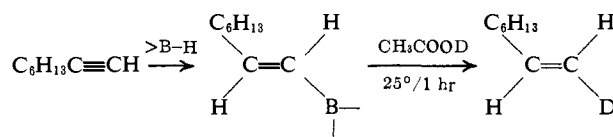
(11) G. Zweifel and H. Arzoumanian, *ibid.*, **89**, 5086 (1967).

(12) G. Zweifel, A. Horng, and J. T. Snow, *ibid.*, **92**, 1427 (1970).

(13) G. Zweifel, J. Plamondon, and J. T. Snow, to be published.

pendent of the aldehyde recovered) of the distribution of boron in the monohydroboration products, the vinylboranes were treated with acetic acid- d_1 . The olefins formed were examined for the distribution of deuterium by nmr.

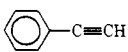
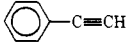
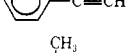
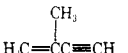
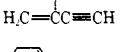
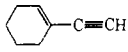
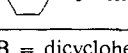
Monohydroboration of 1-octyne with dicyclohexylborane¹⁴ or thexylborane⁷ in tetrahydrofuran at 0° in 1:1 and 2:1 ratio, respectively, resulted in complete utilization of the available hydride. The nmr spectra of both vinylboranes formed indicated a *trans* relationship of the two vinyl protons, arising from a *cis* addition of B-H to the triple bond.¹⁵ Deuterolysis of either vinylborane with acetic acid- d_1 afforded deuterated 1-octene in better than 85% yields. Examination of the deuterated alkene by nmr revealed that at least 95% of the deuterium had been attached at the terminal carbon of the double bond. Both ir and nmr data were con-



sistent with the structure of *trans*-1-octene-1- d , confirming the previously observed retention of configuration in protonolysis reactions involving vinylboranes.⁵

It has been reported that the hydroboration of phenylacetylene with disiamylborane followed by consecutive treatment of the intermediate vinylborane with bromine and with aqueous sodium hydroxide yields *trans*- β -bromostyrene.⁸ To obtain more information concerning the stereoselectivity and the direction of addition of alkylboranes to this alkyne the reactions of phenylacetylene with dicyclohexylborane and with thexylborane in tetrahydrofuran have now also been carried out.¹⁶ The nmr spectra of the resultant vinyl-

Table I. Monohydroboration of Terminal Acetylenes and Enynes with Dicyclohexylborane and Thexylborane

Vinylborane derived from	Hydroborating agent ^a	Yield of olefin	Number of H's at the β position ^b (± 0.04 H)
$\text{C}_6\text{H}_{13}\text{C}\equiv\text{CH}$	DCB ^c	94	0.96
	TB ^d	85	1.02
	DCB ^e	93	1.02
	TB ^d	87	0.96
	DCB ^c	92	1.02
	TB ^d	87	1.03
	DCB ^c	87	0.98
	TB ^d	90	0.98

^a DCB = dicyclohexylborane; TB = thexylborane. ^b $\text{DCH}_2=\text{CH}_2\text{R}$. The number of H's at the β position of the deuterioolefins resulting from the deuterolysis of the intermediate vinylboranes with acetic acid- d_1 was obtained by nmr integration of the proton signals relative to CHCl_3 as internal standard. ^c The hydroboration was carried out at 0° for 2 hr. ^d The hydroboration was carried out at 0° for 1 hr. ^e The hydroboration was carried out at 0° for 1 hr, then at 25° for 1 hr.

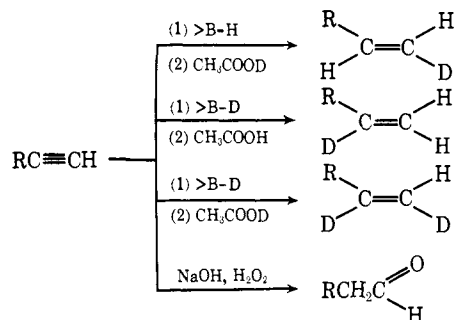
(14) G. Zweifel, N. R. Ayyangar, and H. C. Brown, *J. Amer. Chem. Soc.*, **85**, 2072 (1963).

(15) Similarly, the nmr spectrum of the vinylborane derived from the hydroboration of 1-hexyne with 4,4,6-trimethyl-1,3,2-dioxaborinane in ether at 98–100° for 15 hr was consistent with a *cis* addition of B-H to the triple bond: W. G. Wood and P. L. Strong, *ibid.*, **88**, 4667 (1966).

(16) It is noteworthy that the hydroalumination of phenylacetylene with dialkylaluminum hydrides in a hydrocarbon solvent gives, besides the vinylalane, 25% of the metallated alkyne: T. R. Surtees, *Aust. J. Chem.*, **18**, 14 (1965).

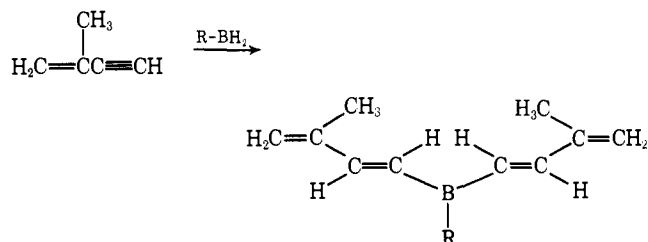
boranes were again consistent with a *cis* addition of B-H to the triple bond. Deuterolysis of both vinylboranes with acetic acid- d_1 yielded over 85% *trans*- β -deuteriostyrene containing at least 95% of the deuterium at the terminal carbon of the double bond. A summary of the experimental results is shown in Table I.

It is evident that monohydroboration of terminal alkynes with dicyclohexylborane or thexylborane proceeds in a highly regiospecific and stereoselective manner to afford high yields of the mono- or divinylboranes.¹⁷ These intermediates may be converted into olefins, deuterated olefins of predictable stereochemistry, or aldehydes⁵ *via* the protonolysis (deuterolysis) and oxidation reactions, respectively.



Monohydroboration of Enynes. Dienylboranes have recently been shown to be of considerable value for use as intermediates in the synthesis of dienes.¹⁰ Thus, we were prompted to extend our study on directive effects in the hydroboration of triple bonds to those in enynes. Based on rate studies with disiamylborane, Brown and Moerikofer¹⁸ have suggested that it should be possible to achieve the selective hydroboration of a triple bond in the presence of nearly any type of double bond, other than a simple, unhindered terminal double bond.

Monohydroboration of isopropenylacetylene with dicyclohexylborane or thexylborane afforded, after deuterolysis of the intermediate dienylboranes,¹⁹ *trans*-3-methyl-1,3-butadiene-1- d in excellent yields. The addition of B-H to the triple bond is highly regiospecific, placing the boron exclusively at the terminal carbon of the acetylene group.²⁰



Similarly, controlled addition of the dicyclohexyl- and thexylboranes to 1-ethynylcyclohexene produces *trans*-

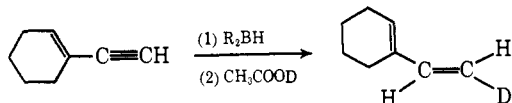
(17) Disiamylborane represents an alternate reagent for the conversion of 1-alkynes into dialkylvinylboranes,⁵ and may possess an advantage over the use of dicyclohexylborane in cases where the products have boiling points similar to that of cyclohexanol.

(18) H. C. Brown and A. W. Moerikofer, *J. Amer. Chem. Soc.*, **85**, 2063 (1963).

(19) A discussion of the absorption spectra of dienylboranes will be reported shortly.

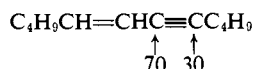
(20) It has been reported that protonolysis of the organoborane derived from isopropenylacetylene with disiamylborane yielded 63% isoprene: V. V. Markova, V. A. Kormer, and A. A. Petrov, *Zh. Obshch. Khim.*, **35**, 1669 (1965).

2-(1-cyclohexenyl)ethenylboranes as evidenced by the formation of *trans*-1-(1-cyclohexenyl)ethylene-2-*d* on deuterolysis with acetic acid-*d*₁.²¹ The results of these studies are also summarized in Table I.



As anticipated, however, a terminal double bond does compete with a terminal triple bond for the hydroborating agents. Thus, 1-hexen-5-yne was hydroborated with dicyclohexylborane. The reaction mixture was treated with acetic acid and then oxidized with alkaline hydrogen peroxide. Glpc analysis revealed the formation of 1,5-hexadiene (38%), 1-hexene (1%), 1-hexen-5-yne (32%), 5-hexen-1-ol (20%), clearly pointing to some 1,6-diaddition to the enyne system.

Finally, it was recently reported that the addition of 1 equiv of dicyclohexylborane to *cis*-1,4-disubstituted conjugated enynes results in the preferential hydroboration of the triple bond.²² However, in the case of *cis*-5-dodecen-7-yne it was established that the reaction is not regiospecific, placing 30% of the boron at the terminal carbon of the triple bond.²²



Monohydroboration of Unsymmetrically Disubstituted Alkynes. The hydroboration of unsymmetrically disubstituted olefins with borane in tetrahydrofuran exhibits a low regiospecificity for the less substituted carbon of the double bond.²³ In order to ascertain whether borane shows a similar behavior in its addition to triple bonds, we have investigated the monohydroboration of a number of methyl substituted alkynes.

To a solution of the appropriate alkyne in tetrahydrofuran was added at 0° a solution of borane in

Table II. Directive Effects in the Hydroboration of Methyl-Substituted Alkynes and *trans*-Olefins with Borane in Tetrahydrofuran Solution

$\text{RC}\equiv\text{CCH}_3$ or $\text{RCH}=\text{CHCH}_3$ $\text{R} =$	Total yield of ketones, ^a %	O	OH
		$\text{RCH}_2\text{C}\equiv\text{CH}$ in ketone product, %	$\text{RCH}_2\text{CHCH}_3$ in alcohol product, % ^b
<i>n</i> -C ₃ H ₇ -	51	60	54
<i>i</i> -C ₃ H ₇ -	70	75	57
	70	74	
<i>t</i> -C ₄ H ₉ -	80	79	58
	74	26	15

^a In all of the reactions studied glpc examination of the reaction mixtures revealed the presence of unreacted alkynes. This observation, together with the rather low yields of recovered ketones, indicates that the alkynes also partly undergo dihydroboration.
^b Reference 23.

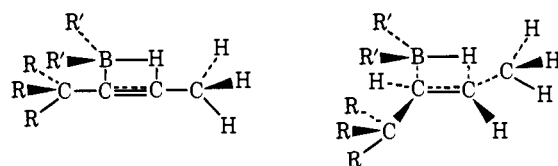
(21) The conversion of 1-ethynylcyclohexene into 1-vinylcyclohexene via the hydroboration-protonolysis reaction has been reported by P. L. Stotter and V. M. Kopal, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. Orgn 83.

(22) G. Zweifel and N. L. Polston, *J. Amer. Chem. Soc.*, **92**, 4068 (1970).

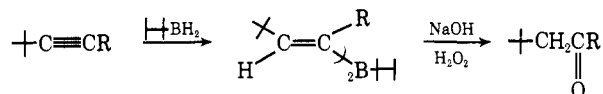
(23) H. C. Brown and G. Zweifel, *ibid.*, **82**, 4708 (1960).

tetrahydrofuran in a 3:1 ratio. The resultant trivinylborane was oxidized with alkaline hydrogen peroxide, and the ketones here formed were analyzed by glpc.²⁴ The experimental results, together with published data for hydroboration of the corresponding olefins, are reported in Table II.

It should be noted that boron exhibits a higher preference for the less substituted carbon of a triple bond as compared with addition to a correspondingly substituted double bond. The addition of borane to alkynes or alkenes must involve at least three stages (not counting the dimeric species). It has been suggested that the four-center²³ and/or π -complex-like²⁵ activated complexes for the hydroboration of olefins have structures resembling the starting materials.²⁶ Based on these models, it appears that steric interactions of the R' groups attached to boron with the larger of the two R groups of the triple or double bond, especially in the third stage of the hydroboration, should be more pronounced with the linear acetylenes.²⁷



It has been reported that thexylborane displays a directive effect similar to that observed with borane in the hydroboration of unsymmetrically disubstituted olefins, leading to a mixture of organoboranes.⁷ A similar trend in selectivity was observed in the monohydroboration of disubstituted acetylenes with thexylborane. Thus, addition of a solution of the monoalkylborane in tetrahydrofuran to a *sec*-alkyl-*n*-alkyl, or to a *tert*-butyl-isopropyl-substituted triple bond in a 1:2 ratio at 0° resulted, after oxidation, in a mixture of ketones (Table III). However, a *tert*-butyl group in competition with an *n*-alkyl group is very effective in directing the boron to the less hindered position of the triple bond as evidenced by the conversion of the resulting divinylthexylboranes into neopentyl *n*-alkyl ketones upon treatment with alkaline hydrogen peroxide. Therefore, the preparation of unsymmetrically disubstituted divinylthexylboranes is confined to starting with *tert*-butyl-*n*-alkylacetylenes.



Although monohydroboration of unsymmetrically disubstituted acetylenes with thexylborane gives mixtures of ketones in most cases, the fact that the ketones were obtained in 85–95% yields indicates that essentially no dihydroboration had occurred. Consequently, vinylboranes derived from the hydroboration



(24) Trivinylboranes are readily converted into deuterated *cis*-olefins upon treatment with acetic acid-*d*₁.⁵ However, the fact that the chemical shifts of the vinyl protons of the olefins are similar makes this procedure unsuitable for the quantitative determination of the distribution of boron.

(25) A. Streitwieser, L. Verbit, and R. Bittman, *J. Org. Chem.*, **32**, 1530 (1967).

(26) J. Klein, E. Dunkelblum, and D. Avrahami, *ibid.*, **32**, 935 (1967).

(27) Although the oxidation of vinylboranes derived from the hydroboration of disubstituted alkynes with borane produces a mixture of ketones, protonolysis of trivinylboranes provides a convenient route to *cis*-olefins.⁵

Table III. Directive Effects in the Hydroboration of Disubstituted Alkynes with Thexyl-, Dicyclohexyl-, and Disiamylborane

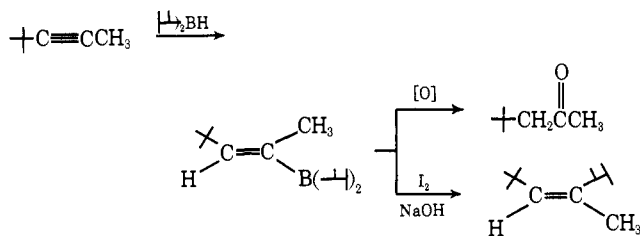
Alkyne (R ₂ C≡CR')		Ketone distribution, % ^a		
R	R'	Thexylborane RCH ₂ CR' O	Dicyclohexylborane RCH ₂ CR' O	Disiamylborane RCH ₂ CR' O
<i>n</i> -C ₃ H ₇ -	CH ₃ -	61	67	61
<i>i</i> -C ₃ H ₇ -	CH ₃ -	81	92	93
	CH ₃ -	78	92	91
<i>tert</i> -C ₄ H ₉ -	CH ₃ -	97 ^c	97 ^c	97 ^c
	CH ₃ -	57	71	81
<i>i</i> -C ₃ H ₇ -	<i>n</i> -C ₄ H ₉ -	72	85	87
<i>tert</i> -C ₄ H ₉ -	<i>n</i> -C ₄ H ₉ -	97	99	99
<i>tert</i> -C ₄ H ₉ -	<i>i</i> -C ₃ H ₇ -	75	96	99

^a The total yields of ketones in all cases were greater than 85%. ^b Per cent in ketone product. ^c The ketones could not be separated by glpc. However, the methyl protons of the *tert*-butyl group of the two ketones had different chemical shifts, and thus it was possible to determine the ratio of the two isomers within $\pm 3\%$ by nmr methods.

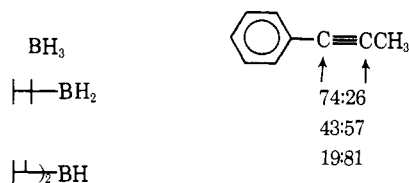
of alkynes with thexylborane are well suited for the preparation of *cis*-olefins when treated with acetic acid.

It was anticipated that dialkylboranes would provide more steric control over the direction of hydroboration of unsymmetrically disubstituted alkynes as compared with borane or thexylborane. Accordingly, we undertook a study of the monohydroboration of a number of representative disubstituted alkynes with dicyclohexylborane and disiamylborane. The resultant vinylboranes were oxidized, and the ketones obtained were examined by glpc.

The experimental results, which are summarized in Table III, clearly indicate that addition of the dialkylboranes occurred predominantly in one direction, placing the boron at the less hindered of the two carbon atoms, except in the cases of 2-hexyne and 1-phenylpropyne. Moreover, both hydroborating agents manifest nearly the same regiospecificity for unsymmetrically disubstituted alkynes. It is evident that such control in the direction of hydroboration is exceedingly valuable for the synthesis of a large variety of disubstituted vinylboranes, which may be converted into highly substituted ketones or trisubstituted olefins.⁹



Finally, the direction of addition of various hydroborating agents to 1-phenylpropyne remains to be considered. The results are summarized below. It ap-



pears that in the absence of large steric requirements on the part of the hydroborating agent, the direction of ad-

dition of boron to the alkyne may be controlled by electronic factors. However, in the case of the sterically more hindered mono- and dialkylboranes, steric factors overshadow the electronic factors, thus directing the boron to the less hindered methyl-substituted carbon of 1-phenylpropyne.

Experimental Section²⁸

Hydroborating Agents. Diborane, generated from boron trifluoride etherate and sodium borohydride, was bubbled through a solution of sodium borohydride in diglyme before being passed into freshly distilled tetrahydrofuran.^{2b} The resultant borane-tetrahydrofuran solution was standardized by decomposing aliquots of the solution with a 1:1 mixture of water-glycerol and measuring the hydrogen evolved.

Disiamylborane was prepared by adding 50 ml of a 2 M solution of borane in tetrahydrofuran to a precooled solution (-10 to 0°) of 2-methyl-2-butene (0.205 mol) in tetrahydrofuran (15 ml). The reaction mixture was stirred at $0-5^\circ$ for 2 hr, then standardized as described above.

Following a similar experimental procedure, cyclohexene was converted into dicyclohexylborane. The resulting suspension of dicyclohexylborane was stirred at $0-5^\circ$ for 1 hr prior to its use.

Thexylborane was prepared by slowly adding 50 ml of a 2 M solution of borane in tetrahydrofuran to a solution of 2,3-dimethyl-2-butene (0.10 mol) in 10 ml of tetrahydrofuran while maintaining the temperature during the addition between -10 and 0° . The reaction mixture was kept at $0-5^\circ$ for 1 hr before being standardized.

Alkynes. Commercial samples of 2-hexyne, 1-octyne, 4-methyl-2-pentyne, 1-hexen-5-yne, 3,3-dimethyl-1-butyne, cyclohexylacetylene (Farchan Chemical Co.), 1-phenylpropyne, and 3-methyl-1-buten-3-yne (Chemical Samples Co.) were utilized without further purification. 1-Ethynylcyclohexene²⁹ and 2,2,5-trimethyl-3-hexyne³⁰ were prepared according to published procedures.

1-Cyclohexylpropyne,³¹ 4,4-dimethyl-2-pentyne,³² 2-methyl-3-octyne,³³ and 2,2-dimethyl-3-octyne³⁴ were synthesized in better

(28) Infrared spectra were obtained on a Beckman IR-8 spectrophotometer. Nmr spectra were run on a Varian Associates Model A-60 spectrometer using tetramethylsilane (TMS) as an internal standard. Chemical shift values are reported in parts per million (δ) downfield from TMS.

(29) J. C. Hamlet, H. B. Henbest, and E. R. H. Jones, *J. Chem. Soc.*, 2652 (1951).

(30) G. K. Helmkamp, F. L. Carter, and H. J. Lucas, *J. Amer. Chem. Soc.*, 79, 1306 (1957).

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(32) H. N. Miller, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Org. Chem.*, 19, 1882 (1954).

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than 80% yields by alkylation of the appropriate lithium acetylides with methyl iodide and *n*-butyl bromide, respectively. The following procedure for the preparation of 2,2-dimethyl-3-octyne is representative. To a solution of 12.3 g (0.15 mol) of 3,3-dimethyl-1-butyne in 150 ml of diglyme was added dropwise at -25 to -15° (Dry Ice-acetone bath) 95 ml of a 1.75 *M* solution of methyllithium (0.165 mol). After allowing the reaction mixture to come to room temperature, the ether was removed under reduced pressure (20 mm), and the resultant clear solution was treated with 22.8 g (0.165 mol) of *n*-butyl bromide. When the initial exotherm had subsided, the resulting mixture was heated at 80 – 90° for 4 hr,³⁵ allowed to come to room temperature, and then was diluted with 150 ml of water. The organic phase formed was separated, and the aqueous phase was extracted with *n*-pentane. In order to remove the diglyme the combined extracts were washed six times with water. The product was distilled through a Vigreux column to give 19.9 g (96%) of 2,2-dimethyl-3-octyne: bp 85 – 86° (100 mm); n_D^{25} 1.4190 [lit.³⁴ bp 79° (70 mm); n_D^{25} 1.4270].

Monohydroboration of 1-Octyne. To a suspension of dicyclohexylborane (20 mmol) in tetrahydrofuran was added at -10 to 0° a solution of 1-octyne (2.21 g, 20 mmol) in tetrahydrofuran. The reaction mixture was maintained at 0 – 5° for 2 hr. The nmr spectrum of the resulting clear solution exhibited the following proton absorptions: δ 6.24 (1 H, d, $J = 18$ Hz, $\text{BCH}=\text{CHR}$) and 6.84 ppm (1 H, doublet of triplets, $J = 6$ Hz, $\text{BCH}=\text{CHCH}_2\text{R}$).

Deuterolysis of the dicyclohexyl(*trans*-1-octen-1-yl)borane with 6 ml of acetic acid- d_1 at 25° for 1 hr, followed by oxidation of the resulting dicyclohexylborinate with alkaline hydrogen peroxide, afforded, by glpc analysis, 94% 1-octene. The reaction mixture was then distilled and a sample of *trans*-1-octene- $1-d$ was isolated by glpc: n_D^{25} 1.4078; ir (CCl_4) 980, 1620, 2265, and 3030 cm^{-1} ; nmr (CCl_4) δ 5.82 (1 H, m, $\text{DHC}=\text{CHCH}_2-$), 4.94 (1 H, doublet of triplets, $J = 17$ and 1.5 Hz, $\text{DHC}=\text{CHCH}_2-$), 1.7–2.4 (2 H, m, $=\text{CCH}_2$), and 0.6–1.7 ppm (11 H, aliph).

Integration of the vinyl protons using chloroform as an internal standard revealed the presence of 1.02 H at the 1 position and 0.96 H at the 2 position.

By the same general procedure a standard solution of thexylborane in tetrahydrofuran (20 mmol) was added at -5 to 0° to a solution of 1-octyne (40 mmol) in tetrahydrofuran (5 ml). Deuterolysis of the resulting divinylthexylborane with 10 ml of acetic acid- d_1 yielded 85% *trans*-1-octene- $1-d$ containing 1.08 H at the 1 position and 1.02 H at the 2 position.

Monohydroboration of Phenylacetylene. A solution of phenylacetylene (2.04 g, 20 mmol) in 10 ml of tetrahydrofuran was added at -10 – 0° to a suspension of dicyclohexylborane (20 mmol) in tetrahydrofuran. The reaction mixture was stirred at 0 – 5° for 1 hr, then at 25° for 1 hr. The nmr spectrum of the resultant vinylborane displayed one vinyl proton absorption at δ 6.97 ppm (1 H, d, $J = 18$ Hz). The other vinyl proton was hidden beneath the phenyl ring protons (δ 7.2–7.7 ppm).

The reaction mixture was treated successively with acetic acid- d_1 (10 ml) and alkaline hydrogen peroxide. Glpc analysis of the organic phase revealed a 93% yield of styrene. The olefin was isolated by preparative glpc: n_D^{25} 1.5421; ir (CCl_4) 690, 970, 980, 1490, and 1610 cm^{-1} ; nmr (CCl_4) δ 7.1–7.7 (5 H, m, arom), 6.67 (1.02 H, doublet of triplets, $J = 17.5$ and 1.5 Hz, $\text{C}_6\text{H}_5\text{CH}=\text{CHD}$), and 5.61 ppm (1.00 H, d, $\text{C}_6\text{H}_5\text{CH}=\text{CHD}$). Integration of the absorption for the proton at the benzylic position of *trans*- β -deuteriostyrene using the phenyl ring protons as an internal standard revealed the presence of 1.02 H.

Phenylacetylene (40 mmol) in tetrahydrofuran (5 ml) was converted into bis(*trans*- β -stryl)thexylborane by treatment with a solution of thexylborane (20 mmol) in tetrahydrofuran. The vinylborane was diluted with 10 ml of acetic acid- d_1 , and then oxidized with alkaline hydrogen peroxide. After work-up, glpc analysis revealed an 87% yield of *trans*- β -deuteriostyrene containing 0.97 H at the benzylic carbon of the double bond.

(35) For the preparation of 1-cyclohexylpropyne and 4,4-dimethyl-2-pentyne, where methyl iodide was used as the alkylating agent, the reaction mixtures were maintained at 25 – 30° for 1 hr.

The results of these deuterolysis experiments are summarized in Table I.

Monohydroboration of Enynes. To a suspension of dicyclohexylborane (20 mmol) in tetrahydrofuran was added at -5 to 0° a solution of 2-methyl-1-buten-3-yne (1.32 g, 20 mmol) in tetrahydrofuran (10 ml). The reaction mixture was maintained at 0 – 5° for 2 hr, then treated successively with acetic acid- d_1 (6 ml) and alkaline hydrogen peroxide. Glpc analysis of the organic extract revealed a 92% yield of isoprene. The pure diene was isolated by preparative glpc: n_D^{25} 1.4180; ir (CCl_4) 845, 890, 980, 1578, and 2270 cm^{-1} ; nmr (CCl_4) δ 1.82 (3 H, t, $J = 1$ Hz, $-\text{CH}_3$), 4.95 (2 H, s, $\text{H}_2\text{C}=\text{C}$), 5.12 (1 H, d, $J = 17$ Hz, $\text{C}=\text{CHD}$), and 6.41 ppm (1 H, doublet of triplets, $J = 17$ and 1.5 Hz, $\text{CH}=\text{CHD}$). Integration of the absorption for the proton at the 2 position of *trans*-3-methyl-1,3-butadiene- $1-d$ using the CH_3 protons absorption as an internal standard indicated the presence of 1.02 H.

The addition of thexylborane (20 mmol) to 2-methyl-1-buten-3-yne (40 mmol) at -5 to 0° yielded, after deuterolysis of the resulting vinylborane, 87% *trans*-3-methyl-1,3-butadiene- $1-d$. The nmr spectrum of the diene revealed 1.03 H at the 2 position.

Hydroborations of 1-ethynylcyclohexene with the dicyclohexyl- and thexylboranes were carried out as described for 2-methyl-1-buten-3-yne. The vinylboranes formed were treated with acetic acid- d_1 . For the pure *trans*-1-(1-cyclohexenyl)ethylene- $2-d$: n_D^{25} 1.4975; ir (CCl_4) 815, 975, 1580, 1640, and 2270 cm^{-1} ; nmr (CCl_4) δ 1.5–2.5 (8 H, alkyl protons), 4.99 (1 H, d, $J = 18$ Hz, $\text{C}=\text{CHD}$), 5.72 (1 H, broad, ring vinyl proton), and 6.30 ppm (1 H, d, $-\text{CH}=\text{CHD}$). The deuterium distribution was determined by nmr using the ring vinyl proton as an internal standard.

A summary of the experimental results obtained from the hydroboration-deuterolysis reaction of these enynes is shown in Table I.

The hydroboration of 1-hexen-5-yne with dicyclohexylborane was carried out as described for 2-methyl-1-buten-3-yne. Protonolysis of the organoborane with acetic acid at 0° for 1 hr, followed by oxidation with alkaline hydrogen peroxide, afforded, by glpc analysis, 1,5-hexadiene (38%), 1-hexene (1%), 1-hexen-5-yne (32%), 5-hexen-1-ol (20%), and cyclohexanol (92%).

Monohydroboration of Disubstituted Alkynes. The following general procedures for the hydroboration of disubstituted alkynes with various hydroborating agents are representative.

To a suspension of dicyclohexylborane (11 mmol) in tetrahydrofuran was added at -5 to 0° a solution of the appropriate alkyne (10 mmol) in tetrahydrofuran (10 ml). The reaction mixture was maintained at 0 – 5° for 1 hr and at 25° for 1 hr. The resulting vinylborane was oxidized by adding to the reaction mixture 4 ml of 3 *N* sodium hydroxide and 4 ml of 30% hydrogen peroxide. The cyclohexanol and the ketone products formed were extracted with ether. The yield and distribution of ketones were determined by glpc using an internal standard as reference. The ketones were isolated by preparative glpc, and their physical constants and spectral properties were compared with those of authentic samples.

Similarly, a solution of disiamylborane (11 mmol) in tetrahydrofuran was added to the alkyne (10 mmol) contained in tetrahydrofuran (10 ml). The reaction mixture was maintained at 0 – 5° for 1 hr before being treated with alkaline hydrogen peroxide. In the case of *tert*-butylisopropylacetylene, the hydroboration was carried out at 0 – 5° for 1 hr, then at 25° for 1 hr. The distribution of the isomeric ketones was determined by glpc.

The hydroborations of alkynes (20 mmol) in tetrahydrofuran (10 ml) with thexylborane (10 mmol) were carried out at 0 – 5° for 1 hr, except in the case of *tert*-butylisopropylacetylene where the mixture was allowed to remain for 1 additional hr at room temperature.

A summary of experimental results of the distribution of ketones derived from the hydroborations of alkynes with dicyclohexyl-, disiamyl-, and thexylboranes is shown in Table III.

Finally, a solution of borane (5.3 mmol) in tetrahydrofuran was added to a solution of the alkyne (15 mmol) in tetrahydrofuran (10 ml). The reaction mixture was kept at 0 – 5° for 1 hr before being oxidized. The yield and distribution of the ketones produced were determined by glpc. A summary of the experimental results obtained is shown in Table II.