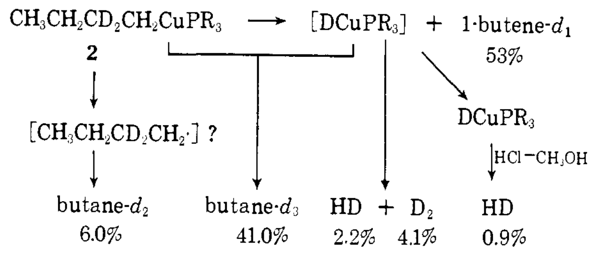
ether) of **2** in the presence of 1 equiv of $HCuP(n\text{-}Bu)_3$,[8] followed by quenching of the reaction mixture with methanolic HCl, yielded, in addition to H_2, 29.7% of HD, the product expected from protonolysis of $DCuP(n\text{-}Bu)_3$.[8] The ability of copper(I) hydride to reduce **1** to butane under the conditions used for the thermal decomposition reactions was established by the isolation of butane-d_1 (24%) together with butane-d_0 (34%) and 1-butene-d_0 (42%) from thermolysis of **1** in the presence of 1.4 equiv of $DCuP(n\text{-}Bu)_3$.[9] Thus, copper(I) hydride *is* formed in the thermal decomposition of **1**; moreover, copper hydride *does* reduce **1**, in a reaction whose rate appears to be competitive with the rate of its formation from **1**. These data are those expected on the basis of the mechanism represented by eq 1 and 2. The absence of HD among the products from thermolysis of **1** in the presence of added D_2 effectively excludes a possible alternative to eq 2 involving thermolysis of the CuH intermediate to yield H_2 and subsequent hydrogenolysis of **1** to form *n*-butane and to regenerate CuH.

To establish the site of elimination of hydrogen from **1**, the alkene products of thermal decomposition of *n*-butyl-1,1-d_2-(tri-*n*-butylphosphine)copper(I) (**3**) and **2** were compared. Decomposition of **3** yields 1-butene-d_2 uncontaminated by -d_1 or -d_0 species, while decomposition of **2** yields 1-butene-d_1. These observations are consistent only with β-hydride elimination occurring without prior scrambling of the deuterium label between α and β positions.

The complete products of decomposition of **2**, together with a schematic rationalization of the paths by which they are formed, are outlined in Scheme I. It is not presently clear whether the small amounts of butane-d_2 and HD formed in this reaction are the result of radical side reactions involving **2** and $DCuP(n\text{-}Bu)_3$, respectively, or whether they reflect an unidentified reaction generating copper *hydride*.[10,11] Regardless, this product distribution is clearly consistent with the proposed mechanism.

Scheme I



A mechanism for thermal decomposition of **1** involving copper hydride elimination has good precedent in related studies of rhodium,[12] platinum,[13] and lithium[14] alkyls. However, this study provides the first easily interpretable example in which subsequent reaction of a metal hydride and its parent metal alkyl is important in determining the products of a thermal decomposition. Similar mechanisms may be involved in the variety of thermal reactions of other transition metal alkyls which yield approximately equal quantities of alkene and alkane.

[9] Previously reported studies have established that reaction of copper(I) hydride and copper(I) alkyls takes place by a nonradical mechanism.[8a]

[10] Oxidative addition of a carbon–hydrogen bond of solvent or of tri-*n*-butylphosphine to d^{10} copper(0) might provide a method of introducing hydrogen into Scheme I. For relevant oxidative additions to d^8 metals, see F. Piacenti, *et al.*, *J. Amer. Chem. Soc.*, **90**, 6847 (1968); S. Bresadola, P. Rigo, and A. Turco, *Chem. Commun.*, 1205 (1968); G. W. Parshall, W. H. Knoth, and R. A. Schunn, *J. Amer. Chem. Soc.*, **91**, 4990 (1969).

[11] Adventitious hydrolysis of 2 is not responsible for the formation of *n*-butane-d_2: thermal decomposition of **2** (1.00 mmol) prepared from a solution of $[ICuPBu_3]_4$ (0.27 mmol) which was previously treated with methyllithium (0.08 mmol) to remove impurities capable of protonolyzing organocopper reagents produced *n*-butane-d_3 (41%), *n*-butane-d_2 (8%), and 1-butene-d_1 (51%).

[12] R. Cramer, *Accounts Chem. Res.*, 1, 186 (1968).

[13] J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc., A*, 190 (1968), and references therein.

[14] R. A. Finnegan and H. W. Kutta, *J. Org. Chem.*, 30, 4138 (1965).

[15] (a) National Institutes of Health Predoctoral Fellow, 1967–1970; (b) National Science Foundation Predoctoral Fellow, 1963–1967; (c) National Institutes of Health Predoctoral Fellow, 1966–1969.

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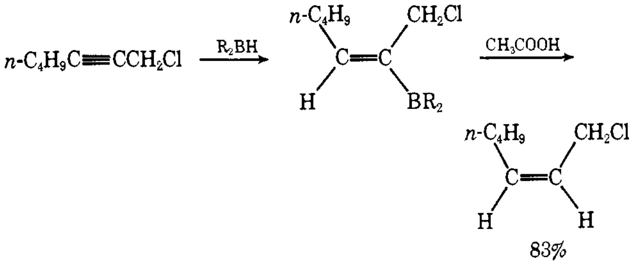
The Hydroboration of Substituted Propargyl Chlorides. A Convenient Synthesis of Terminal Allenes[1]

Sir:

In the course of exploring the chemistry of organoboranes derived from functionally substituted alkynes we have investigated the unsaturated chloroorganoboranes derived from the reactions of dialkylboranes with 1-chloro-2-alkynes. We now wish to report that these organoboranes afford, after treatment with aqueous sodium hydroxide, good yields of the corresponding allenes which are free from by-products.

A study of the stoichiometry of hydroboration of 1-chloro-2-heptyne with disiamylborane in tetrahydrofuran solvent at 0° revealed that the reaction proceeds readily to the monohydroboration stage. The intermediate organoborane is stable in tetrahydrofuran solution, as evidenced by its conversion to isomerically pure *cis*-1-chloro-2-heptene on protonolysis with glacial acetic acid.[2]



In order to determine the position of the boron in the monohydroboration product, 1-chloro-2-heptyne was allowed to react with 1 equiv of the disiamylborane (R_2BD) derived from 2-methyl-2-butene and deuterioborane. The resultant organoborane was protonolyzed with acetic acid, and the *cis*-1-chloro-2-heptene obtained was treated with ozone in cyclohexane. The ozonide was diluted with ether and then reduced with lithium aluminum hydride.[3] Nmr examination of the 1-pen-

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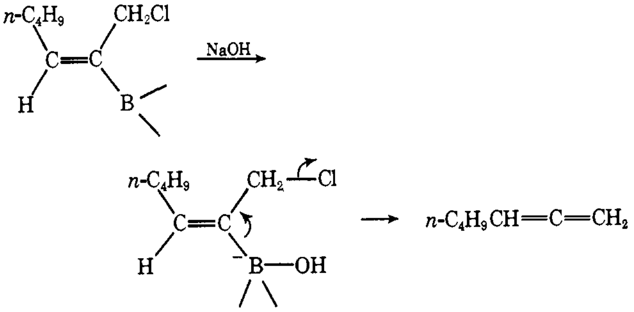
[1] This research was supported by the National Science Foundation through Grant No. GP-9398.

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

[3] J. A. Sousa and A. Bluhm, *J. Org. Chem.*, **25**, 108 (1960).

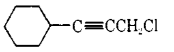
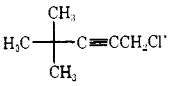
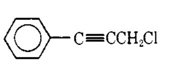
tanol and 2-chloroethanol formed revealed that 95 ± 5% of one deuterium had been attached at the 2 position of the double bond in the chloroheptene. This points to a marked directive influence of the chlorine substituent.[4]

It was anticipated that the monohydroboration product derived from 1-chloro-2-heptyne might undergo β elimination to give 1,2-heptadiene on treatment with a strong base, and this was borne out by experiment. Addition of aqueous sodium hydroxide to the β-boron derivative resulted in a facile elimination to give, by glpc analysis, an 83% yield of the anticipated terminal allene.[5]



The above hydroboration–elimination sequence has also been applied successfully to a number of other 1-chloro-2-alkynes[6] of varying structures. For all of the cases, the allenes formed were free of by-products. The experimental results are summarized in Table I.

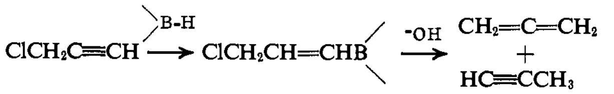
Table I. Yields of Terminal Allenes Obtained from 1-Chloro-2-alkynes *via* the Hydroboration–Elimination Reactions in Tetrahydrofuran Solvent

Propargyl chloride	Yield of allene, %[a,b]
$n\text{-}\mathrm{C_4H_9C{\equiv}CCH_2Cl}$	64[c] (83)
	72 (93)
	65[d] (92)[d]
	73 (91)

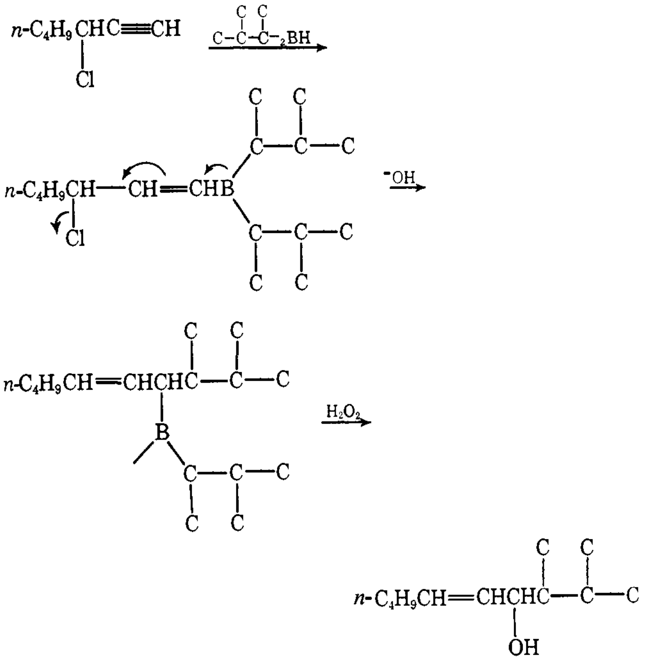
[a] The values given in parentheses were obtained by glpc analysis using an external standard. The other values are isolated yields. [b] The spectral data were in agreement with the assigned structures. [c] Dicyclohexylborane was used as the hydroborating agent (ref 5). [d] Since the tetrahydrofuran solvent interfered with the isolation of the allene it was replaced by diglyme, after completion of the hydroboration reaction.

The simplicity of the procedure is illustrated by the following example. A solution of 2-methyl-2-butene (0.145 mol) in tetrahydrofuran (10 ml) was placed in a 200-ml flask equipped with a thermometer, a pressure-equalizing funnel, and a magnetic stirrer. The flask was immersed in a $\mathrm{CCl_4}$–Dry Ice bath and hydroboration was achieved by adding 39 ml of a solution of borane (73 mmol) in tetrahydrofuran maintaining the temperature between −10 and 0°. The reaction mixture was stirred at 0–5° for 2 hr. To the disiamylborane (73 mmol) formed was added at −20 to −10° ($\mathrm{CCl_4}$–Dry Ice bath) 10 ml of a solution of 1-chloro-3-cyclohexyl-2-propyne (70 mmol) in tetrahydrofuran. The reaction mixture was stirred at 0–5° for 30 min. The resulting organoborane was treated at −20 to −10° with 30 ml of 6 *N* sodium hydroxide, then stirred vigorously at 0–5° for 30 min. The disiamylborinate formed was oxidized at 25–35° by adding 18 ml of 30% hydrogen peroxide. The products were extracted repeatedly into *n*-pentane. Distillation through a tantalum spiral column yielded, besides 3-methyl-2-butanol, 72% of 3-cyclohexyl-1,2-propadiene: bp 56–57° (15 mm); $n^{23}\mathrm{D}$ 1.4786 [lit.[7] bp 155–156° (755 mm), $n^{20}\mathrm{D}$ 1.4658]; ir (neat) 1960, 1690 (C=C=C), and 840 $\mathrm{cm^{-1}}$ (=$\mathrm{CH_2}$); nmr ($\mathrm{CCl_4}$) δ *ca.* 5.0 (m, 1, C*H*=C=C), 4.58 (m, 2, C=C=C*H*$_2$), and *ca.* 1.5 (m, 11, C*H*, C*H*$_2$).

It has been reported that the hydroboration of propargyl chloride with dialkylboranes affords, after treatment of the monohydroboration product with aqueous sodium hydroxide, a 95:5 mixture of allene and propyne.[8] Therefore, it was of interest to explore the



possibility of also preparing terminal allenes from 3-chloro-1-alkynes. Thus, 3-chloro-1-heptyne was allowed to react with 1 equiv of disiamylborane. The monohydroboration product formed was treated with



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(4) A similar directive effect is observed in the hydroboration of crotyl chloride with borane. Here, the addition of boron proceeds essentially 100% to the 2 position. However, the saturated hydroboration product undergoes spontaneous elimination to give, after rehydroboration–oxidation, mainly 1-butanol: H. C. Brown and R. M. Gallivan, *J. Amer. Chem. Soc.*, **90**, 2906 (1968).

(5) In order to facilitate the isolation of the allene product, the disiamylborinate group was oxidized to 3-methyl-2-butanol. Unfortunately, the 1,2-heptadiene and the 3-methyl-2-butanol were observed to have similar boiling points. However, this difficulty is readily circumvented by using dicyclohexylborane for the hydroboration.

(6) The substituted propargyl chlorides were prepared in better than 65% yields by the following reaction sequence

$$\mathrm{RC{\equiv}CH} \xrightarrow{\mathrm{CH_3Li}} \mathrm{RC{\equiv}CLi} \xrightarrow{\mathrm{(CH_2O)}_x} \mathrm{RC{\equiv}CCH_2OH} \xrightarrow[\mathrm{(C_4H_9)_3N}]{\mathrm{SOCl_2}} \mathrm{RC{\equiv}CCH_2Cl}$$

(7) R. J. Lewina and D. H. Trachtenberg, *Zh. Obshch. Khim.*, **6**, 764 (1936).

(8) P. Binger and R. Köster, *Angew. Chem.*, 74, 652 (1962).

6 N sodium hydroxide, followed by the addition of 30% hydrogen peroxide. Glpc examination of the ether extract, however, revealed that the yield of 1,2-heptadiene amounted to less than 1%. After removal of the solvents, distillation gave 68% of 2,3-dimethyl-*trans*-5-decen-4-ol. Apparently, one siamyl group migrates in the presence of base to the adjacent carbon with concurrent shift of the double bond and loss of chloride. Oxidation of the allyl boron intermediate gives the allylic alcohol. It should be noted here that saturated γ-chloroorganoboranes undergo cyclization to give cyclopropane derivatives on treatment with bases.[9]

It is evident that monohydroboration of substituted propargyl chlorides should be of wide utility in synthesizing allenes, *cis*-allyl chlorides, and allyl alcohols. We continue to explore the potentialities of organoboranes derived from propargyl chlorides, including 1,3-disubstituted propargyl chlorides, in organic syntheses.

(9) M. F. Hawthorne, *J. Amer. Chem. Soc.*, **82**, 1886 (1960); P. Binger and R. Köster, *Tetrahedron Lett.*, 156 (1961); P. Binger and R. Köster, *Angew. Chem.*, **74**, 652 (1962); H. C. Brown and S. P. Rhodes, *J. Amer. Chem. Soc.*, **91**, 2149 (1969).

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Alkyldiazenes

Sir:

The first alkyldiazene to be directly observed (*t*-butyldiazene) was found to disappear rather quickly.[1] A later report suggested that methyldiazene was "surprisingly stable."[2] We now report a complete series of alkyldiazenes, for which we have made the following observations: (a) all alkyldiazenes, like alkenyldiazenes[3] and aryldiazenes,[4a,d,5] undergo a bimolecular reaction with themselves; (b) the rate of the bimolecular reaction is fairly sensitive to the nature of the alkyl group; (c) methyldiazene has a bimolecular decomposition rate about like that of phenyldiazene;[4a–d,6] (d) all alkyldiazenes react rapidly with oxygen, as do all other monosubstituted diazenes;[1,3–6] and (e) the hydrocarbon (RH) derived from the bimolecular reaction of alkyldiazenes (RN=NH) is formed in less than quantitative yield.

Alkyldiazenes were generated either by elimination[7–10] or decarboxylation[1,4–6] (eq 1–3). The methyl alkyldiazenecarboxylates were derived from the corresponding hydrazo compounds by oxidation for all alkyl

$$\mathrm{TsNHNH_2} \xrightarrow[\mathrm{LiH}]{\mathrm{RX}} \mathrm{RN(Ts)NH_2} \xrightarrow[\mathrm{EtOH}]{0.1\ M\ \mathrm{OEt^-}} \mathrm{RN{=}NH} \qquad (1)$$

$$\mathrm{Ts} = p\text{-}\mathrm{CH_3C_6H_4SO_2};\ \mathrm{R} = \mathrm{CH_3,\ CH_3CH_2,\ (CH_3)_2CH}$$

$$\mathrm{RNHTs} \xrightarrow[\mathrm{OEt^-\text{–}EtOH}]{\mathrm{NH_2OSO_3^-Na^+}} [\mathrm{RN(Ts)NH_2}] \longrightarrow \mathrm{RN{=}NH} \qquad (2)$$

$$\mathrm{R} = \mathrm{CH_3,\ CH_3CH_2,\ (CH_3)_2CH,\ (CH_3)_3C,}\ c\text{-}\mathrm{C_3H_5},\ c\text{-}\mathrm{C_6H_{11}}$$

$$\mathrm{RN{=}NCOOCH_3} \xrightarrow{\mathrm{KOH}} \mathrm{RN{=}NCOO^-K^+} \xrightarrow[\mathrm{EtOH}]{\mathrm{ImH^+Cl^-}} \xrightarrow{-\mathrm{CO_2}} \mathrm{RN{=}NH} \qquad (3)$$

$$\mathrm{Im} = \text{imidazole};\ \mathrm{R} = \mathrm{CH_3},^{11}\ \mathrm{CH_3CH_2,\ (CH_3)_2CH,\ (CH_3)_3C,}\ c\text{-}\mathrm{C_3H_5},\ c\text{-}\mathrm{C_6H_{11}}$$

groups.[12]

Quantitative conversion of the methyl ester to the carboxylate ion with sodium hydroxide was utilized for the measurement of absorption coefficients of the anions with R = c-C_3H_5, c-C_6H_{11}, $(CH_3)_3C$, and $(CH_3)_2CH$. Under the same conditions, the esters with R = CH_3 and CH_3CH_2 partially isomerized to the hydrazone, so that it was necessary to assume that the absorption coefficient for the anions, $CH_3N{=}NCOO^-$ and $CH_3CH_2N{=}NCOO^-$, were the same as that of $(CH_3)_2CHN{=}NCOO^-$.

Absorption coefficients for the n → π^* transition of the alkyldiazenes were obtained through quantitative decarboxylation of the anion by treatment with imidazolium hydrochloride in ethanol.[4a,b] With the aid of these reasonably accurate absorption coefficients, it was possible to obtain rate constants for the bimolecular decompositon of the alkyldiazenes. Spectroscopic and kinetic data are listed in Table I.

Table I. Properties of Alkyldiazenes

RN=NH, R =	λ_{max}, Å (ϵ_{max})[a]	10^2k_2,[a,b] M^{-1} sec^{-1}	Bimolecular reaction product[c]
c-C_3H_5	3490 (28)	1.5	Cyclopropane (>50%)
CH_3	3610 (18)[d]	3.0	
CH_3CH_2	3670 (18)	42	
$(CH_3)_2CH$	3680 (20)	60	Propane (75%)
c-C_6H_{11}	3680 (20)	58	Cyclohexane (82%)[e]
$(CH_3)_3C$	3750 (17)	280	Isobutane (75%)

[a] In ethanol solution. [b] Rate constants are approximately ±25%, including constants for diazenes generated by more than one method. [c] Identification by complete infrared spectra; yield by measurement of a number of infrared band intensities and pressure. [d] Taken as equal to that of ethyldiazene. [e] Identification by glpc retention time; yield by peak area comparison with that of an authentic sample of similar concentration.

Previous studies on the products of the bimolcular reaction of aryldiazenes[4d,5] and alkenyldiazenes[3] indicated that the major product in all cases but one[15]

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(1) P. C. Huang and E. M. Kosower, *J. Amer. Chem. Soc.*, **89**, 3911 (1967).

(2) M. N. Ackermann, J. L. Ellenson, and D. H. Robinson, *ibid.*, **90**, 7173 (1968). We have confirmed their preparation of methyldiazene from CH_3NHOH and $NH_2OSO_3^-Na^+$ and have found that the bimolecular disappearance rate constant in ethanol or acetonitrile is similar to that found for methyldiazene generated in other ways.

(3) T. Tsuji and E. M. Kosower, *ibid.*, **91**, 3375 (1969).

(4) (a) P. C. Huang and E. M. Kosower, *ibid.*, **89**, 3910 (1967); (b) *ibid.*, **90**, 2354 (1968); (c) *ibid.*, **90**, 2362 (1968); (d) *ibid.*, **90**, 2367 (1968).

(5) E. M. Kosower, P. C. Huang, and T. Tsuji, *ibid.*, **91**, 2325 (1969).

(6) E. M. Kosower and P. C. Huang, *ibid.*, **87**, 4645 (1965).

(7) J. S. McFayden and T. S. Stevens, *J. Chem. Soc.*, 584 (1936).

(8) A. Nickon and A. Sinz, *J. Amer. Chem. Soc.*, **82**, 753 (1960).

(9) A. Nickon and A. S. Hill, *ibid.*, **86**, 1152 (1964).

(10) D. J. Cram and J. S. Bradshaw, *ibid.*, **85**, 1108 (1963).

(11) Slight change in procedure for this alkyl derivative.

(12) Methyl alkyldiazenecarboxylates vary greatly in stability. All compounds exhibited either nmr or mass spectrum consistent with structure. The compounds $RNHNHCOOCH_3$ (R = CH_3, CH_3CH_2, $(CH_3)_2CH$, c-C_6H_{11}) were prepared by hydrogenation of the appropriate carbomethoxyhydrazones over Raney nickel. Methyl cyclopropyldiazanecarboxylate (*cf.* ref 4c for nomenclature) was prepared from cyclopropylamine by the method of Lwowski[13] and methyl *t*-butyldiazanecarboxylate was made by the method of Chaco and Rabjohn.[14] Details will be given in the full publication.

(13) W. Lwowski and T. J. Maricich, *J. Amer. Chem. Soc.*, **87**, 3630 (1965).

(14) M. C. Chaco and N. Rabjohn, *J. Org. Chem.*, **27**, 2765 (1962).

(15) The bimolecular reaction of 4-nitrophenyldiazene yielded 35% nitrobenzene, the major product being 1,2-bis(4-nitrophenyl)diazane.[5]