(12) Benzene (Burdick and Jackson) and $C_2Cl_3F_3$ (Freon 113, Matheson) were shaken with H_2SO_4, passed through basic alumina, and distilled. Dichloromethane (Mallinckrodt Spectrograde) was distilled from P_2O_5. Carbon tetrachloride (Mallinckrodt Spectrograde) was irradiated (Pyrex) in the presence of benzophenone, passed through basic alumina, and distilled.

(13) Addition of ~10^{-7} M $CuCl_2$ (with 1% MeOH for solubility) increased the rate of decomposition of 1 in CH_2Cl_2 by a factor of ~10.

(14) Invoking the steady-state approximation for [acetone*] leads to eq 3, where, under the experimental conditions, [1] is constant.[8] For the case where $k_L \ll k_D$, eq 3 reduces to eq 2.

$$I \propto k_A [1][k_L/(k_L + k_D)] \qquad (3)$$

(15) N. J. Turro and A. Devaquet, *J. Am. Chem. Soc.*, **97**, 3859 (1975).

(16) (a) Calculated values of ΔH_f° follow: dioxetanone 1, ca. −88 kcal/mol;[16b] tetramethyldioxetane, −68.8 kcal/mol.[16c] (b) W. H. Richardson and H. E. O'Neal, *J. Am. Chem. Soc.*, **94**, 8665 (1972); (c) W. H. Richardson and H. E. O'Neal, *ibid.*, **92**, 6553 (1970).

(17) Fellow of the Alfred P. Sloan Foundation, 1977–1979.

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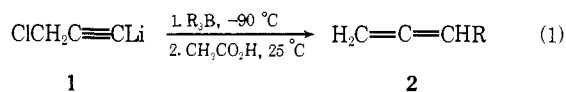*University of Illinois, Urbana, Illinois 61801*

Synthesis of Homopropargylic and α-Allenic Alcohols from Lithium Chloropropargylide, Trialkylboranes, and Aldehydes[1]

Sir:

During the past few years there has been a surge of interest in development of novel routes for α-allenic alcohols. This has arisen as a consequence of the α-hydroxyallene structural feature being contained in many natural substances[2] and synthetic physiologically active compounds.[3] A number of the latter have proven to be powerful hypertensive and antiinflammatory agents.

Recently we reported that protonation with acetic acid of organoboranes derived from trialkylboranes and lithium chloropropargylide (1) afforded alkylallenes 2 (eq 1).[4,5] In

$$\text{ClCH}_2\text{C}\!\equiv\!\text{CLi} \xrightarrow[\text{2. CH}_3\text{CO}_2\text{H, 25 °C}]{\text{1. R}_3\text{B, −90 °C}} \text{H}_2\text{C}\!=\!\text{C}\!=\!\text{CHR} \qquad (1)$$

$$\mathbf{1} \qquad\qquad\qquad\qquad\qquad \mathbf{2}$$

exploring the chemistry of organoboranes leading to **2**, we have now uncovered operationally simple, high-yield syntheses of homopropargylic (**4**) and α-allenic alcohols (**5**) via sequential treatment of **1** with trialkylboranes and aldehydes. The overall reactions represent efficient 1,3- and 1,1-dialkylations, respectively, of the readily available propargyl chloride, and thus pave the way to α-allenic and homopropargylic alcohols not readily accessible via previously available methodologies.[6]

The most remarkable feature of these synthetic transformations is the discovery that the alcohol which is specifically formed depends on the temperature at which the organoborane precursor is maintained prior to its reaction with the aldehyde.
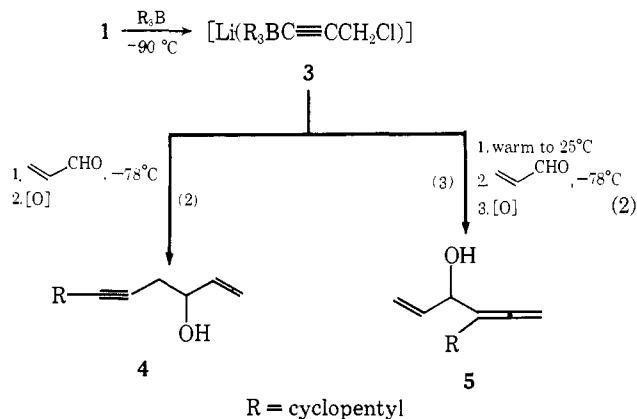
$$\mathbf{1} \xrightarrow[\text{−90 °C}]{\text{R}_3\text{B}} [\text{Li}(\text{R}_3\text{BC}\!\equiv\!\text{CCH}_2\text{Cl})] \qquad (2)$$

$$\mathbf{3}$$

R = cyclopentyl

Table I. Yield of Homopropargylic and α-Allenic Alcohols

| | | isolated yields, %[a,b] | |
| | | $\text{RC}\!\equiv\!\text{CCH}_2\text{C-}$ | $\text{R}^1(\text{HO})\text{CHC-}$ |
$\text{R}_3\text{B, R}$	$\text{R}^1\text{CHO, R}^1$	(OH)HR[1]	(R)=C=CH_2
cyclopentyl	C_2H_5	89 (99)	80 (99)
	c-C_6H_{11}	88 (99)	86 (99)
	t-C_4H_9	86 (100)	79 (96)
	C_6H_5	86 (100)	85 (99)
	$H_2C\!=\!CH$	75 (97)	84 (100)
	(E)-CH_3-$CH\!=\!CH$	84 (100)	84 (100)
2-methylcyclopentyl	i-C_3H_7		78 (96)[c]
cyclohexyl	C_2H_5		77 (98)
n-C_6H_{13}	C_2H_5	85 (99)[d]	73 (98)[d]

[a] The numbers in parentheses are isomeric purities. [b] The spectral data of the alcohols obtained were consistent with the assigned structures. [c] The stereochemistry of the 2-methylcyclopentyl moiety has not been determined. [d] The alcohol contained 7% of the isomeric alcohol resulting from the reaction of 1 with the organoborane derived from addition of BH_3 to the 2 position of 1-hexene.

Thus, addition of the carbonyl compound to the organoboron intermediate at −78 °C produces, after oxidative workup, nearly exclusively the homopropargylic alcohol (eq 2). On the other hand, if the organoborane is first brought to room temperature and then treated with the aldehyde at −78 °C, the α-allenic alcohol is obtained essentially free of contamination by the corresponding homopropargylic alcohol (eq 3).

A typical procedure for the preparation of the homopropargylic alcohol **4** is as follows. Propargyl chloride (20 mmol) in THF (10 mL) was cooled to −90 °C (liquid nitrogen-methanol bath) and then reacted with a solution of butyllithium (20 mmol, 1.6 M) in hexane while the temperature was maintained below −80 °C during the addition. The reaction mixture was stirred for an additional 10 min and, then, to the resultant lithium chloropropargylide (**1**, 20 mmol) was added a solution of tricyclopentylborane (20 mmol, 1.66 M) in THF by a double-ended needle[7] over a 15-min period, with the temperature being kept below −80 °C during the addition. The mixture was stirred for 30 min at −78 °C (dry ice–acetone bath) and then treated with a solution of 2-propenal (20 mmol) in THF (4 mL) while the temperature was maintained below −67 °C during the addition. After the mixture was stirred for 1 h at −70 °C, it was brought to room temperature (30 min), treated with methanol (10 mL), and oxidized at 30–50 °C with 3 N NaOH (7.2 mL) and 30% H_2O_2 (4.8 mL). Ether extraction, drying ($MgSO_4$), and distillation afforded 2.44 g (75%) of **4**.
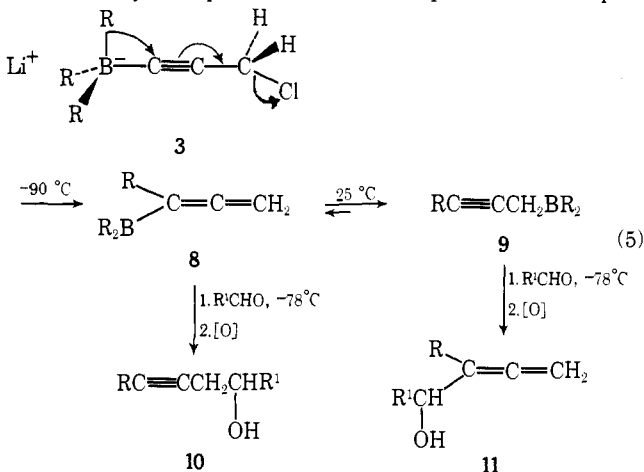
The corresponding α-allenic alcohol **5** was obtained by a slight modification of the experimental procedure described for the preparation of **4**. Thus, the organoborane derived from **1** and tricyclopentylborane was allowed to warm to room temperature prior to addition of the 2-propenal at −78 °C. A summary of the experimental results obtained for the syntheses of various homopropargylic and α-allenic alcohols is given in Table I.

It is gratifying to note that the preparations of both types of alcohols accommodate a variety of structural features in both the alkylborane and aldehyde moieties.[8] Moreover, α,β-unsaturated aldehydes, such as acrolein and crotonaldehyde, react exclusively in a 1,2 fashion as exemplified by the preparation of the alcohols **4** and **5**. However, it should be pointed out that the procedures utilize only one of the three available alkyl groups of the trialkylborane. Attempts to circumvent this by using *B*-alkyl-9-borabicyclo[3.3.1]nonanes[9]

resulted in the preferential transfer of the 9-BBN moiety. On the other hand, the use of thexylchloroborane (*B*-chloro(1,1,2-trimethylpropyl)borane,[10] 6) as the hydroborating agent provided a partial solution to the problem. Thus, treatment of a terminal olefin such as 1-octene with 6 followed by addition of 2 molar equiv of 1 at −90 °C induced preferential migration of the primary group as evidenced by the formation of alcohol 7 (76%) on reaction of the intermediate organoborane with propanal (eq 4).[11] However, extension of the reaction to *B*-chlorothexylalkylboranes derived from 6 and disubstituted internal olefins resulted in extensive migration of the thexyl group.

$$C_8H_{17} \text{—}\!\!\!\equiv\!\!\!\text{—} \quad \overset{\displaystyle}{\underset{OH}{}} \qquad (4)$$

7
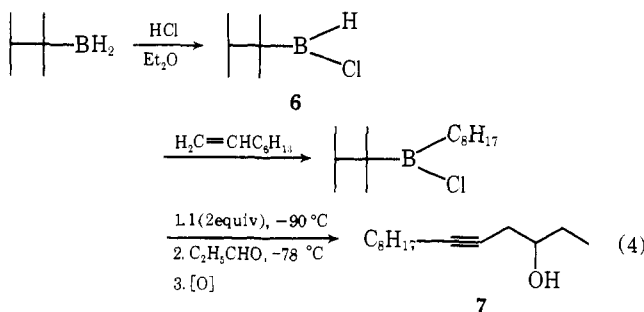
The reactions leading to the homopropargylic and α-allenic alcohols may be depicted as follows in eq 5. The ate complex

3

$$\xrightarrow{-90\,°C} \quad \overset{R}{\underset{R_2B}{>}}\!\!C\!\!=\!\!C\!\!=\!\!CH_2 \quad \underset{-90\,°C}{\overset{25\,°C}{\rightleftharpoons}} \quad RC\!\!\equiv\!\!CCH_2BR_2 \qquad (5)$$

8   **9**

1. R¹CHO, −78 °C
2. [O]

$$RC\!\!\equiv\!\!CCH_2CHR^1 \qquad\qquad \overset{R}{\underset{R^1CH}{>}}\!\!C\!\!=\!\!C\!\!=\!\!CH_2$$
$$\quad\; | \qquad\qquad\qquad\qquad\quad |$$
$$\;\; OH \qquad\qquad\qquad\qquad\; OH$$

10   **11**

3 formed by reaction of the trialkylborane with **1** at −90 °C undergoes a spontaneous anionotropic rearrangement in which one alkyl group migrates from boron to the adjacent carbon concomitant with an electron-pair shift and loss of chloride to produce the allenic borane **8**.[4,12] Treatment of **8** at −78 °C with the aldehyde results in an allenic–propargylic rearrangement to give, after oxidative workup, the homopropargylic alcohol **10**. However, if the allenic borane **8** initially formed is allowed to warm, it rearranges to the thermodynamically more stable propargylic borane **9**.[9,13] This in turn reacts with the carbonyl group of aldehydes at −78 °C with bond transpositions to produce the α-allenic alcohol **11**.[14,17]

In connection with the mechanistic scheme proposed in eq 5, it should be noted that the isomeric purities of the α-allenic alcohols **11** obtained depend not only on the temperature at which the aldehyde is added to the reaction mixture but also on the aldehyde structure. Use of relatively unhindered aldehydes such as propanal leads to the corresponding alcohols **11** in >90% isomeric purities regardless of whether the reaction is carried out at −78 or at 25 °C. On the other hand, a marked temperature effect upon the isomeric purities of the α-allenic alcohols **11** is observed with sterically more hindered aldehydes. Thus, reaction of the equilibrated organoborane with pivalaldehyde at −78 °C afforded, after workup, the α-allenic alcohol **11** (R = cyclopentyl; R¹ = *t*-C₄H₉). However, addition of the same aldehyde to the organoborane at 25 °C resulted

in the preferential formation of **10** (R = cyclopentyl; R¹ = *t*-C₄H₉) containing only 11% of the corrresponding α-allenic alcohol **11**. These results suggest that allenic boranes are more reactive than are the corresponding propargylic boranes toward aldehydes, especially with sterically more hindered aldehydes. At low temperature, equilibration of the organoboranes **8** and **9** is sufficiently slow that the thermodynamically more stable propargylic borane **9** can effectively be trapped by the aldehyde to give the α-allenic alcohol **11**. However, at elevated temperatures, equilibration of the organoboranes is fast, hence allowing the more reactive allenic borane **8** to compete favorably with **9** for the aldehyde.

References and Notes

(1) This research was supported by the National Science Foundation through Grant CHE76-03738.
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(3) E. Galantay, I. Bacso, and R. V. Coombs, *Synthesis*, 344 (1974), and references therein.
(4) T. Leung and G. Zweifel, *J. Am. Chem. Soc.*, **96**, 5620 (1974).
(5) Disubstituted alkylallenes may be prepared via sequential treatment of ethynylalkanol acetates with *n*-butyllithium, trialkylboranes, and acetic acid: M. M. Midland, *J. Org. Chem.*, **42**, 2650 (1977).
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(8) Preliminary investigations have revealed that utilization of ketones instead of aldehydes leads to mixtures of homopropargylic and α-allenic alcohols.
(9) H. C. Brown, E. F. Knights, and C. G. Scouten, *J. Am. Chem. Soc.*, **96**, 7765 (1974).
(10) *B*-Chlorothexylborane was prepared by adding 1 equiv of an ethereal solution of hydrogen chloride to thexylborane in THF at 0 °C.
(11) GLC examination revealed the presence of ∼7% of the thexyl migrated product.
(12) Owing to the complexity of the NMR and IR spectra resulting from the presence of THF, information as to the structure of the intermediate organoborane has been impossible for us to obtain thus far.
(13) We previously proposed that the allenes produced via protonation of the reaction mixtures derived from **1** and trialkylboranes with acetic acid at room temperature were derived from allenic boranes **8**. However, in view of the results obtained in the present study, it would appear that the actual precursors are the propargylic boranes **9**. Work is currently in progress to resolve this uncertainty.
(14) It has previously been shown that aldehydes react with dibutyl allenyl- and dibutyl propargylboronates via rearrangement.[15,16] In these cases, however, the presence of the butoxy substituents on boron inhibited equilibration of the allenyl- and propargylboronates.
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(16) The allenyl- and propargylboronate esters were prepared from methylborate and the corresponding unsaturated organoaluminum or magnesium compounds: E. Favre and M. Gaudemar, *C. R. Hebd. Sceances Acad. Sci., Ser. C*, **262**, 1332 (1966).
(17) For recent alternative syntheses of propargylboronate esters, see J. Blais, A. L'Honore, J. Soulie, and P. Cadiot, *J. Organomet. Chem.*, **78**, 323 (1974); H. C. Brown et al., *J. Org. Chem.*, **42**, 4088 (1977).

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Crystal and Molecular Structure of a Biscyclopentadienyluranium(IV) Phosphoylide Dimer, [μ-(CH)(CH₂)P(C₆H₅)₂U(C₅H₅)₂]₂·(C₂H₅)₂O

Sir:

In recent years there have been a number of reports[1-3] describing the coordination chemistry of phosphorus ylides with various main-group and transition metal atoms. The unusual stability of the metal carbon σ bonds in the known ylide complexes prompted us to investigate them as ligands toward actinides, for which no such complexes have been reported. In this communication we report the synthesis and crystal structure of the first actinide phosphoylide complex, [μ-(CH)(CH₂)P(C₆H₅)₂U(C₅H₅)₂]₂, which possesses an unusual