aqueous HCl, and extracted with ether; the extract was dried over $MgSO_4$ and evaporated to give crude 3-hydroxyphenylmethylthienyl-2-carboxylic acid (4), which was characterized as its methyl ester prepared from 4 by treatment with diazomethane: NMR ($CDCl_3$) $\delta$ 7.02 (d, 1 H, $J$ = 5 Hz, 4-thienyl-H), 6.42 (s, 1 H, PhCH), 3.7 (s, 3 H, $OCH_3$). The crude acid (200 mg) was dissolved in 20 mL of benzene, *N,N*-dicyclohexylcarbodiimide (170 mg) was added, and the mixture was refluxed for 30 min and evaporated. The residue was subjected to preparative thin-layer chromatography ($SiO_2$, $CH_2Cl_2$:EtOAc, 9:1) to give 160 mg of the lactone 5 as an oil: IR ($CHCl_3$) 1760 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.86 (d, 1 H, $J$ = 5 Hz, 5-thienyl-H), 7.35 (s, 5 H, Ph), 6.95 (d, 1 H, $J$ = 5 Hz, 4-thienyl-H), 6.31 (s, 1 H, PhCH). Anal. Calcd for $C_{12}H_8O_2S$: C, 66.63; H, 3.73. Found: C, 66.45; H, 4.11.

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**Registry No.**—**1**, 62521-42-0; **2**, 62521-43-1; **3**, 62521-44-2; **4**, 62521-45-3; **4** methyl ester, 62521-46-4; **5**, 62521-47-5; 2-thiophenecarboxyl chloride, 5271-67-0; 2-amino-2-methyl-1-propanol, 124-68-5; benzaldehyde, 100-52-7.

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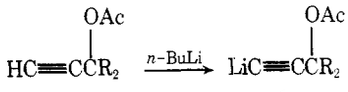
# Communications

## Preparation of Allenes and Acetylenes from Ethynylalkanol Acetates via Organoboranes

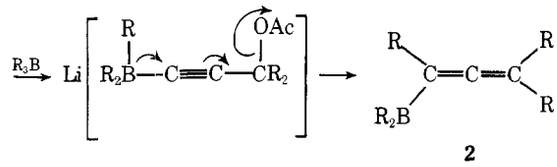
*Summary:* Sequential treatment of an ethynylalkanol acetate with *n*-butyllithium and a trialkylborane produces an allenic borane, $R_2BRC{=}C{=}CR_2$, which may be protonated to form either an allene, $RHC{=}C{=}CR_2$, or an acetylene, $RC{\equiv}CCHR_2$.

*Sir:* Allenes have conventionally been prepared from ethynylalkanol acetates through organocopper reagents.[1] However, these organocopper reagents are generally prepared from reactive organometallics which preclude the presence of many functional groups. Allenes may also be prepared from organoboranes by treatment with the lithium salt of propargyl chloride.[2] While the organoboranes can accommodate a wide variety of functional groups,[3] it is not clear that the reaction could be accomplished in the presence of these functional groups. Furthermore, this process is limited by the availability of propargyl chlorides.

We have now found that the use of the more readily available ethynylalkanol acetates[4] provides a general method for making allenic boranes (2) and, thus, allenes and acetylenes.



1

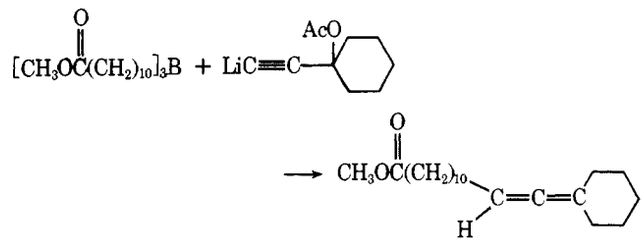


2

Formation of the desired lithium salt (1) was accomplished without interference by the acetate group by reaction of the ethynylalkanol acetate with *n*-butyllithium at low temperature (−78 or −120 °C). Addition of a trialkylborane followed by warming to room temperature and then protonation with acetic acid results in the formation of an allene.[2,5,6] The overall sequence results in the transformation of a ketone or aldehyde to an allene.

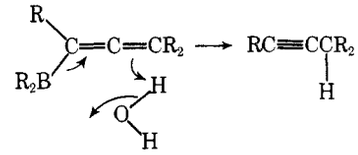
$$R_3B + HC{\equiv}CH + O{=}CR'_2 \rightarrow RHC{=}C{=}CR'_2$$

The reaction is quite general both with respect to the organoborane and the ethynylalkanol acetate (Table I). Slightly better results were usually obtained when the reaction was run at −120 rather than −78 °C. Finally, the reaction is able to accommodate an ester functionality in the organoborane with no difficulty.



3

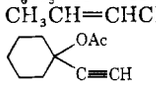
Allenic boranes have the potential of reacting as allylic boranes, which are known to undergo a number of reactions that are unusual for vinyl- or alkylboranes, such as addition to carbonyl compounds or protonation with water.[7] Addition of water to 2 results in the exclusive formation of an acetylene. As with allylic boranes, the product presumably results from protonation with rearrangement via a cyclic process.



The overall transformation results in the reductive alkynylation of a ketone.

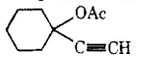
$$R_3B + HC{\equiv}CH + O{=}CR'_2 \rightarrow RC{\equiv}CCR'_2 \quad (\text{H on the CR'}_2)$$

Table I. The Conversion of Ethynylalkanol Acetates to Allenes

| $R_2'C(OAc)C{\equiv}CH$ | % yield, $RHC{=}C{=}CR_2'$[a] | | |
|---|---|---|---|
| | $n$-$Bu_3B$[b] | $i$-$Bu_3B$[b] | $sec$-$Bu_3B$[b] |
| $(CH_3)_2C(OAc)C{\equiv}CH$ | 80 | 90 | 76 |
| $n$-$C_5H_{11}CH(OAc)C{\equiv}CH$ | 87 (78), 90[c] | 76, 92[c] | 80, 92[c] |
| $C_6H_5CH(OAc)C{\equiv}CH$ | 77, 94[c] | 70, 91[c] | 82, 90[c] |
| $C_6H_5CH{=}CHCH(OAc)C{\equiv}CH$ | (64)[c] | | |
| $CH_3CH{=}CHCH(OAc)C{\equiv}CH$ | 87 (72)[c] | | |
|  | 82 | 78 (75) | 81 (73) |

[a] % yield based on acetate by VPC (isolated yields are in parentheses). [b] $R_3B$. [c] −120 °C, other reactions at −78 °C.

Table II. The Conversion of Ethynylalkynol Acetates to Acetylenes

| $R_2'C(OAc)C{\equiv}CH$ | $R_3B$ | % yield,[a] $RC{\equiv}CCHR_2'$ |
|---|---|---|
| $n$-$C_5H_{11}CH(OAc)C{\equiv}CH$ | $n$-$Bu_3B$ | 87 (78) |
| $C_6H_5CH(OAc)C{\equiv}CH$ | $n$-$Bu_3B$ | 91 |
| $C_6H_5CH(OAc)C{\equiv}CH$ | $sec$-$Bu_3B$ | 91 |
| $CH_3CH{=}CHCH(OAc)C{\equiv}CH$ | $n$-$Bu_3B$ | (60) |
|  | $n$-$Bu_3B$ | 84 (70) |

[a] % yield based on acetate by VPC (isolated yields are in parentheses). All reactions were run at −78 °C.

The reaction is quite general and gives high yields of the acetylene (Table II).

The following procedure for the preparation of methyl cyclohexylidenetetradeca-12,13-dienoate (**3**) is representative. The trialkylborane was prepared[3a] in a 50-ml flask under nitrogen from 15.5 mmol of borane–methyl sulfide and 50 mmol of methyl 10-undecenoate using 20 mL of tetrahydrofuran, 5 mL of diethyl ether, and 5 mL of pentane as a solvent.[8] A separate, dry 100-mL flask was flushed with nitrogen and charged with 20 mL of THF, 5 mL of ether, 5 mL of pentane, and 15 mmol of 1-ethynylcyclohexanol acetate. The solution was cooled to −120 °C[8] [petroleum ether (30–60 °C)–isopropyl alcohol–acetone (4:1:1)/1$N_2$]. $n$-Butyllithium, 15 mmol (9.6 mL of a 1.56 M solution in hexane) was added dropwise followed by the dropwise addition of the organoborane solution. The solution was then warmed from −120 °C to room temperature. The solution became slightly cloudy. After 15 min at room temperature, 3 mL of dry acetic acid was added. The mixture was stirred for 15 min and then neutralized (phenolphthalein) with 3 M sodium hydroxide. The aqueous layer was separated, and the THF dried ($K_2CO_3$) and removed under vacuum. Pentane (60 mL) was added, followed by 15 mmol of ethanolamine. The solution was warmed briefly and a heavy solid ethanolamine adduct of $R_2BOH$ was removed by filtration. After removal of the pentane, the residue was distilled to give 3.35 g of product (73%): bp 140–145 °C (0.02 mm); IR (neat) 1950 (allene), 1740 $cm^{-1}$ (carbonyl); $^1H$ NMR ($CCl_4$, TMS) $\delta$ 1.2–2.3 (br m, 30 H), 3.62 (s, 3 H), 4.9 (br m, 1 H). The product contained ~5% isomer resulting from hydroboration at the internal position of methyl 10-undecenoate. No acetylene was detected. Repetition of the reaction at −78 °C resulted in a 61% isolated yield.

The hydrocarbon allenes were conveniently isolated by column chromatography on silica gel or alumina following oxidation of the organoborane by-product. The acetylenes were prepared by substituting water for acetic acid.

This procedure offers a general method for preparing allenic boranes which can be converted to either allenes or acetylenes. Furthermore, the allenic boranes may be extremely versatile intermediates, similar to allylic boranes in their reactions. For example, preliminary experiments have shown that they will add readily to ketones and aldehydes to give homopropargylic alcohols, $RC{\equiv}CCR_2CR'_2OH$.[9] We are continuing to explore these versatile reagents.

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(5) We have previously prepared the allenic boranes, **1** (R = $n$-Bu; R' = $C_6H_5$, H) [IR 1950 $cm^{-1}$; NMR $\delta$ 6.15 (t, $J$ = 3.0 Hz)] by addition of dilithium trialkylboraacetylides, $(R_3BC{\equiv}CLi)Li$, to aldehydes followed by acetylation (M. M. Midland, the 172nd National Meeting of the American Chemical Society, San Francisco, Aug 29–Sept 3, 1976).
(6) In a few cases up to 10% acetylene was formed.
(7) B. M. Mikhailov, *Organomet. Chem. Rev. A*, 1 (1972).
(8) G. Köbrich and H. Trapp, *Chem. Ber.*, **99**, 680 (1966).
(9) In contrast to our results, Zweifel has found that allenic boranes react with aldehydes to give allenic alcohols.[2]

**M. M. Midland**
*Department of Chemistry, University of California*
*Riverside, California 92521*
*Received March 23, 1977*

## 1,2- and 1,4-Oxides of Azonine. A Unique Synthetic Entry into N-Substituted 1-Pyrindines

*Summary:* The preparation and characterization of three isomeric oxides of azonine, a hitherto unknown $C_8H_8XY$ family of heterobicyclics, and the development of a convenient synthetic scheme for the construction of the interesting, yet rare, N-substituted 1-pyrindine system are described.

*Sir:* We wish to offer brief description of work which led to (i) the synthesis of three isomeric oxides of azonine, a hitherto unknown $C_8H_8XY$ family of diheterobicyclics and (ii) the development of a general synthetic scheme for the construction of the interesting, but rare,[1] N-substituted 1-pyrindine system depicted as **6**.

We discovered that reaction between urethane **1** and $m$-chloroperbenzoic acid (mcpba) leads, in ~55% yield, predominantly[2] to the 1,2-azonine oxide shown as **2**[3] [colorless liquid; $^1H$ NMR (100 MHz, $CDCl_3$) $\tau$ 3.53 (1 H, d, $H^3$, $J_{3,2}$ = 6.5 Hz), 3.75 (1 H, d, $H^5$, $J_{5,6}$ = 11.0 Hz), 3.9–4.3 (4 H, m), 5.73 (2 H, q), 6.62 (1 H, m, $H^1$ or $H^9$), 6.78 (1 H, m, $H^9$ or $H^1$), 8.72 (3 H, t); $^{13}C$ NMR (25 MHz, $CDCl_3$) 57.64 ($C^9$ or $C^1$), 55.76 ppm ($C^9$ or $C^1$); $\lambda_{max}$ ($C_6H_{14}$) 260 nm ($\epsilon$ 2000); $m/e$ 207 ($P^+$,