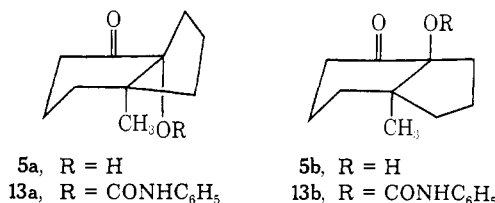


breakdown of a common intermediate<sup>11</sup> such as **12**, leading to the thermodynamic mixture of **5a** and **5b**.

In order to provide additional evidence concerning the nature of this rearrangement, we sought a base labile derivative of **5** which would allow isolation of a single epimer.<sup>12</sup> To this end the mixture of *cis*- and *trans*-**5** obtained from the acyloin reaction was converted to phenylcarbamate **13** by treatment with phenyl isocyanate. The nmr spectrum of **13** showed two methyl singlets occurring at  $\delta$  0.90 and 1.19 in a ratio of 2.1 to 1, respectively, and were attributed to the *trans* and *cis* carbamates. Recrystallization of the carbamate mixture from  $\text{CHCl}_3$ -hexane gave a 15% yield of pure **13b** (mp 108–109°) as determined by nmr. Hydrolysis of **13b** in refluxing methanol-water con-



taining potassium hydroxide for 7 hr gave, after workup a 76% yield of a mixture of **5a** and **5b** in a ratio of 1 to 2.3. The isolation of a mixture of epimers of **5** from the hydrolysis of a single epimer of **13** shows that the *cis* and *trans* forms of **5** are interconvertible under the basic conditions of the hydrolysis and supports the existence of intermediate **12**.

Further work is now in progress on the reactions of acyloins **5a** and **5b**, and studies of the scope of this type of acyloin interaction are in progress.

**Acknowledgment.** This work was partially supported by the National Institutes of Health Grant No. AI 10389.

(11) Similar intermediates have been implicated in rearrangement of bicyclo[2.2.1]heptane systems. See A. Nickon, T. Nishida, and Y. Lin, *J. Amer. Chem. Soc.*, **91**, 6860 (1969), and references cited therein.

(12) Attempts to isolate epimers **5a** and **5b** by gas chromatography under a variety of conditions were unsuccessful.

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## Allenic Boranes. Their Preparation and Conversion into Alkylallenes<sup>1</sup>

Sir:

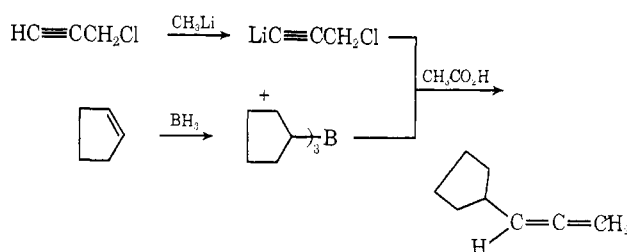
In our continuing investigations of the chemistry of organoboranes derived from functionally substituted acetylenes,<sup>2</sup> we have now uncovered a novel procedure for the preparation of allenic boranes<sup>3</sup> and, *via* their reaction with acetic acid, an operationally simple method for addition of the allene moiety to olefinic

(1) This research was supported by the National Science Foundation through Grant No. GP-26369.

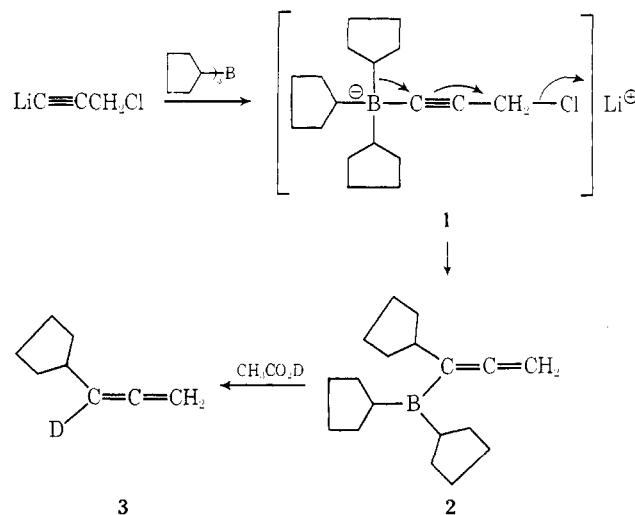
(2) G. Zweifel and H. Arzoumanian, *J. Amer. Chem. Soc.*, **89**, 5086 (1967); J. Plamondon, J. T. Snow, and G. Zweifel, *Organometal. Chem. Syn.*, **1**, 249 (1971); G. Zweifel and A. Horng, *Synthesis*, 672 (1973); *J. Amer. Chem. Soc.*, **96**, 316 (1974).

(3) It has been reported that sequential treatment of propargyl bromide with magnesium and trimethylborate produces a 36% yield of dimethoxyallenylborate [ $\text{CH}_2=\text{C}=\text{CHB}(\text{OCH}_3)_2$ ]. E. Favre and M. Gaudemar, *C. R. Acad. Sci., Ser. C*, **262**, 1333 (1966).

double bonds,<sup>4</sup> as represented by the specific example shown below.



Thus, addition of an equimolar amount of methyl-lithium in ether to propargyl chloride in tetrahydrofuran at  $-70$  to  $-60^\circ$  resulted in quantitative metalation of the acetylenic group. This was evidenced by the amount of methane evolved. The resultant lithium salt of propargyl chloride<sup>5</sup> was immediately treated with a solution of tricyclopentylborane in tetrahydrofuran while maintaining the temperature during the addition between  $-70$  to  $-60^\circ$ . The reaction was allowed to warm up to room temperature, then was examined by nmr and ir. The nmr spectrum revealed only a singlet at  $\delta$  5.65 in the vinyl proton region, and the ir spectrum exhibited an absorption band at  $1950\text{ cm}^{-1}$ . Thus both the nmr and the ir data point to formation of the 1,1-disubstituted 1,2-propadiene **2**.<sup>6</sup> Additional support for the proposed structure of the allenic borane **2** was obtained by its treatment with  $\text{CH}_3\text{COOD}$ . Nmr examination of the 1-cyclopentyl-1,2-propadiene formed indicated nearly exclusive incorporation of one deuterium at the 1-position of the 1,2-diene moiety (**3**).



The reactions leading to **2** may be depicted as follows. The ate complex **1**, formed by the reaction of tricyclopentylborane with the lithium chloropropargylide, undergoes a spontaneous anionotropic rearrangement in which one alkyl group migrates from boron to the

(4) Allenes may also be obtained by aqueous sodium hydroxide treatment of  $\beta$ -chlorovinylboranes, derived from the reaction of dialkylboranes with 1-chloro-2-alkynes. G. Zweifel, A. Horng, and J. T. Snow, *J. Amer. Chem. Soc.*, **92**, 1427 (1970).

(5) Addition of acetone to lithium chloropropargylide at  $-70^\circ$  produced a 90% yield of 1-methyl-5-chloro-3-pentyne-1-ol. Metalation of propargyl chloride with butyllithium has been described by L. Brandsma "Preparative Acetylenic Chemistry," Elsevier, New York, N. Y., 1971, p 77.

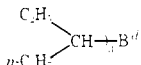
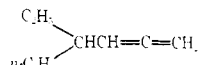

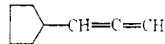

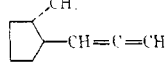

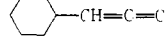
(6) Due to the complexity of the nmr and ir spectra resulting from the presence of THF and ether, no additional information as to other structural features of the allenic borane could be obtained.

adjacent carbon concomitant with an electron pair shift and loss of chloride.

Protonolysis of the allenic borane **2** at 25–30° with acetic acid afforded, after work-up, a 75% isolated yield of cyclopentylallene. However, it should be noted that the allene contained a small amount of methylcyclopentylacetylene (~3%). In exploring the full scope of this novel allene synthesis using acetic acid in the protonolysis step, it was observed that the amount of methylalkylacetylene formed increased markedly when the temperature during the preparation of the lithium chloropropargylide and the ate complex **1** were allowed to rise above –60°. We are currently investigating the nature of the precursor which leads to methylalkylacetylenes.

In order to determine the stereochemistry of the migrating group, tri(2-*trans*-methylcyclopentyl)borane was treated with the lithium chloropropargylide. Acetolysis of the reaction mixture afforded 1-(*trans*-2-methylcyclopentyl)-1,2-propadiene,<sup>7</sup> indicating that the migration of the 2-methylcyclopentyl moiety must have proceeded with retention of configuration. A summary of the experimental results obtained for the synthesis of various allenes is given in Table I.

**Table I.** Yields of Allenes Obtained *via* the Reaction of Lithium Chloropropargylide with Various Trialkylboranes

Trialkylborane	Product allene <sup>a,b</sup>	Isolated yield, %
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> B	<i>n</i> -C <sub>4</sub> H <sub>9</sub> CH=C=CH <sub>2</sub>	73 <sup>c</sup>
		74
		75
		76
		77

<sup>a</sup> The nmr, ir, and mass spectral data for all new compounds reported are consistent with the structures proposed. <sup>b</sup> The allene products were better than 95% pure. <sup>c</sup> Glpc analysis revealed that the 1,2-nonadiene contained approximately 7% of the isomeric allene resulting from the reaction of lithium chloropropargylide with the organoborane derived from addition of BH<sub>3</sub> to the 2 position of 1-hexene. <sup>d</sup> Derived from hydroboration of *trans*-3-hexene.

The following description of the preparation of 1-cyclohexyl-1,2-propadiene is representative. To a solution of cyclohexene (60 mmol) in THF (10 ml) was added a 2 *M* solution of borane (20 mmol) at such a rate as to maintain the temperature at 25–45°. The reaction mixture was stirred at 40–45° for an additional 3 hr before being added to the lithium chloropropargylide.

Propargyl chloride (20 mmol) in THF (10 ml) was placed into a separate flask. The solution was cooled to –70°, then diluted with a 1.6 *M* solution of methyl-lithium (20 mmol) in ether while maintaining the temperature during the addition between –70 and –60°. To the resultant lithium chloropropargylide was added immediately the solution of tricyclohexylborane, keep-

(7) The stereochemistry of the allene follows from its hydrogenation to *trans*-1-methyl-2-propylcyclopentane.

ing the temperature during the addition between –70 and –60°. The reaction mixture was allowed to warm up to room temperature, the THF and ether were removed under reduced pressure, and the residue obtained was diluted with 5 ml of acetic acid. The mixture was stirred at 25–30° for 1 hr and the allene formed was distilled under reduced pressure into a receiver immersed into a Dry Ice–acetone bath. The distillate was neutralized with aqueous sodium hydroxide to remove acetic acid, and the allene was extracted with pentane. After drying with magnesium sulfate, the pentane was removed and the residue was distilled to give 1.9 g (77%) of 1-cyclohexyl-1,2-propadiene; bp 58° (12 mm); *n*<sub>D</sub><sup>25</sup> 1.4862.

Preliminary investigations of the chemistry of allenic boranes have revealed that they react with aldehydes to yield the corresponding allenic alcohols, a reaction which is analogous to that previously encountered with allylic boranes.<sup>8</sup> Thus, dialkyl(1,2-propadienyl)boranes should provide a useful allenic synthon for organic synthesis. We are currently exploring the full scope of the utility of these unsaturated organoboranes in synthesis.

(8) B. M. Mikhailov, *Organometal. Chem. Rev., Sect. A*, **8**, 1 (1972).

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## Photochemical Isomerization of 1-Sila-2,4-cyclohexadienes

Sir:

Photoinduced isomerizations of 1,3-cyclohexadienes and the resulting hexatrienes have been studied extensively.<sup>1</sup> Photochemistry of analogous silacyclohexadienes appeared interesting, since the possible products or intermediates should be elusive silahexatrienes<sup>2</sup> or silacyclopropanes.<sup>3</sup> We report here the first examples of photochemical reactions of 1-sila-2,4-cyclohexadienes.

When an evacuated benzene solution of 1,1-dimethyl-2,5-diphenyl-1-sila-2,4-cyclohexadiene (**1**)<sup>4</sup> was irradiated in an nmr tube,<sup>5</sup> only a single photoproduct (**2**) was detected. After complete disappearance of **1** (40 hr), the mixture was subjected to a preparative tlc on silica gel to

(1) (a) W. G. Dauben, R. C. Williams, and R. D. McKelvey, *J. Amer. Chem. Soc.*, **95**, 3932 (1973); (b) W. G. Dauben, M. S. Kellogg, J. I. Seeman, N. D. Vietmeyer, and P. H. Wendschuh, *Pure Appl. Chem.*, **33**, 197 (1973); (c) A. Padwa, L. Brodsky, and S. Clough, *J. Amer. Chem. Soc.*, **95**, 6767 (1973); (d) S. W. Spangler and R. P. Hennis, *J. Chem. Soc., Chem. Commun.*, 24 (1972).

(2) The transient existence of Me<sub>2</sub>Si=CH<sub>2</sub> was indicated by (a) L. E. Gusel'nikov and M. C. Flowers, *Chem. Commun.*, 864 (1968); (b) M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, 419 (1968); (c) T. J. Barton and C. L. McIntosh, *J. Chem. Soc., Chem. Commun.*, 861 (1972). See also ref 8.

(3) Recently, R. L. Lambert, Jr., and D. Seyferth, *J. Amer. Chem. Soc.*, **94**, 9246 (1972), have reported silacyclopropanes. See also D. Seyferth, C. K. Haas, and D. C. Annarelli, *J. Organometal. Chem.*, **56**, C7 (1973).

(4) Compound **1** was prepared by reaction of 1,4-dithio-1,4-diphenylbutadiene with dimethyl(chloromethyl)chlorosilane in THF: mp 74–76°; δ (CCl<sub>4</sub>) 0.30 (6 H, s, SiMe<sub>2</sub>), 2.00 (2 H, d, H<sub>3</sub>, J<sub>3,4</sub> = 1.5 Hz), 6.41 (1 H, dt, H<sub>1</sub>, J<sub>2,4</sub> = 6.8 Hz, J<sub>4,6</sub> = 1.5 Hz), 6.86 (1 H, d, H<sub>3</sub>, J<sub>3,4</sub> = 6.8 Hz), 7.0–7.5 (10 H, m); λ<sub>max</sub><sup>n-hexane</sup> 230 (12,000), 340 nm (24,000).

(5) Throughout experiments, a 450-W high-pressure mercury arc lamp was used for irradiation with a Pyrex filter.