The Insertion of Alkylidene Groups into Diene Systems. A Convenient Synthesis of Alkylidenecycloalkanes via Monohydroboration of 1-Bromo-1-alkynes with Bis-boracyclanes

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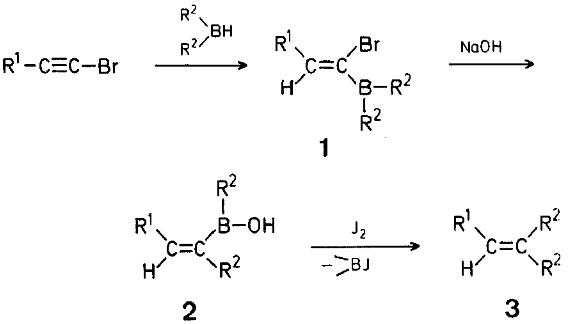
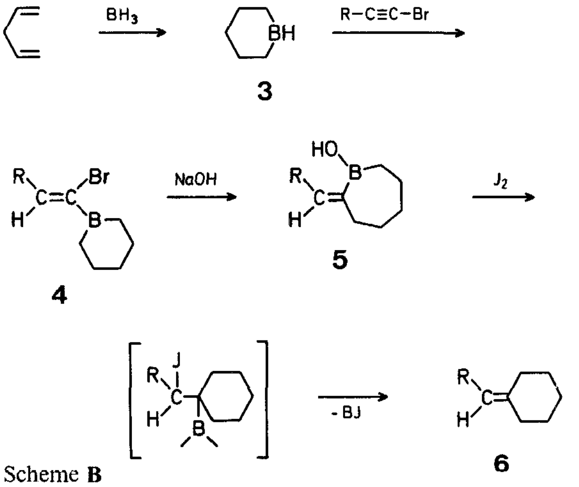
Treatment of 1-bromo-1-alkenyldialkylboranes (**1**) with aqueous sodium hydroxide results in intramolecular displacement of bromine by an alkyl group attached to boron to produce 1,2-dialkyl-substituted vinylborinic acids (**2**)[1]. Addition of iodine to these vinylborinic acids results in migration of the remaining alkyl group on boron to the adjacent carbon to give, after deboronoiodination[2], the corresponding trialkyl-substituted olefins (Scheme A)[3].



Scheme A

Extension of the above sequential alkyl-group migration to B-(1-bromo-1-alkenyl)-boracycloalkanes leads to a novel synthesis of alkylidenecycloalkanes.

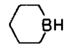
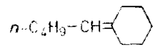
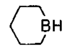
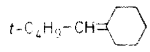
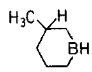
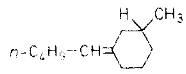
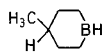
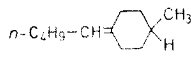
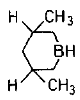
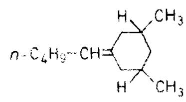
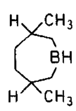
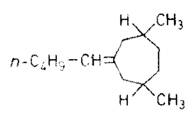
Recently, convenient procedures for the conversion of 1,4-pentadienes[4,5] and 2,5-dimethyl-1,5-hexadiene[5] into the corresponding bisborinanes and bis-[3,6-dimethylborepane], respectively, have been reported. Thus, monohydroboration of 1-bromo-1-hexyne with bisborinane **3** affords the α-bromovinylborane **4** in good yield as evidenced by its conversion to 1-bromo-1-hexene on protonolysis with acetic acid. Treatment of this vinylborane with 6 *N* sodium hydroxide presumably leads to a displacement of bromine by one end of the boracycloalkyl moiety to form the seven-membered ring borepane intermediate **5**. Addition of iodine to **5** then results in migration of the other end of the cycloalkyl chain from boron to the adjacent carbon to give, after deboronoiodination, pentylidenecyclohexane in a 71% yield (**6**, $R = n\text{-}C_4H_9$; Scheme **B**).



Scheme **B**

This reaction exhibits great versatility in that it allows for considerable modification in the starting materials. Thus, similar high yields of alkylidenecyclohexanes are formed whether the alkyl group attached to the triple bond of the 1-bromo-1-alkyne is *n*-butyl or *t*-butyl. Furthermore, substituted bisborinanes, such as bis-[3,5-dimethylborinane][5,6] may also be employed successfully in the reaction. Finally, it was gratifying to note that the reaction may be utilized for construction of cycloheptane ring systems by using bis-[3,6-dimethylborepane][5] as hydroborating agent. A summary of the results obtained in selected examples of these reactions is given in Table 1.

Table 1. Alkylidenecycloalkanes Derived from α-Bromovinylboracycloalkanes

1-Bromo-1-alkyne	Hydroborating Agent	Alkylidenecycloalkane[a]	Yield %
$n\text{-}C_4H_9-C\equiv C-Br$			71[b]
$t\text{-}C_4H_9-C\equiv C-Br$			67
$n\text{-}C_4H_9-C\equiv C-Br$			71[c]
			66
			83[d]
			73[e]

[a] The spectral data for all new compounds reported are consistent with the structures proposed.

[b] Yield by G.L.C. analysis.

[c] This compound is presumed to be a *cis-trans* mixture of isomers.

[d] Ozonolysis of the compound revealed a 39 to 61 mixture of *cis*-3,5-dimethylcyclohexanone and *trans*-3,5-dimethylcyclohexanone.

[e] Ozonolysis of the alkylidenecycloheptane revealed a 35 to 65 mixture of isomeric 3,6-dimethylcycloheptanones.

1-Pentylidene-3,5-dimethylcyclohexane:

Into a dry 100-ml flask equipped with a thermometer, a pressure-equalizing addition funnel, a septum-capped side arm, and a magnetic stirrer was added 1-bromo-1-hexyne[7] (3.22 g, 20 mmol) in tetrahydrofuran. The contents of the flask were cooled to −15°, and hydroboration was achieved by the dropwise addition of a 1.66 *M* solution (12.6 ml) of bis-[3,5-dimethylborinane][5] in tetrahydrofuran (21 mmol of hydride). The resulting solution was allowed to warm slowly to 0° (15 min), and then was stirred for an additional 2 hr at 0–5°. After addition of 5 ml of methanol to decompose any residual hydride, the reaction mixture was cooled to −15° and aqueous 6 *N* sodium hydroxide (10 ml) was added dropwise while maintaining vigorous stirring. The mixture was allowed to come to room temperature, then was again cooled to −15°, and a solution of iodine (5.1 g, 20 mmol) in tetrahydrofuran was added dropwise while maintaining the temperature below 0°. After allowing the reaction mixture to warm to room temperature, excess iodine was decomposed by the addition of aqueous sodium thiosulfate. The olefin product was extracted into pentane, and the pentane extract was washed once with saturated aqueous sodium chloride. After drying with magnesium sulfate, the solvents were removed and the residue distilled; yield: 3.0 g (83%); b.p. 64–67°/1.6 mm; n_D^{24}: 1.4590.

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[3] G. Zweifel, R.P. Fisher, to be published.

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[6] The bisboracyclane presumably is a mixture of *cis* and *trans* isomers.

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