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## REGIO- AND STEREOSPECIFIC SYNTHESIS OF TRIPLY UNSATURATED HYDROCARBONS FROM INTERNAL ENYNYLDIALKYLBORANES

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Internal enynyldialkylboranes give regio- and stereospecifically designed conjugated enynes, bearing an allyl or l-alkynyl group on the internal alkenyl carbon atom, by a coupling reaction with allyl bromide or l-bromo-l-alkynes.

Although the chemistry of alkenylboranes has been developed, alkenylboranes appeared in most papers were confined to terminal ones.<sup>1)</sup> In relation to a synthesis of internal alkenylboranes,<sup>2)</sup> recently the authors synthesized conjugated enynyldialkylboranes by successive reactions of 1-iodo-1-alkynes with dialkylboranes and 1-alkynyllithiums(Eq. 1).<sup>3)</sup>

$$R^{1}C \equiv CI \xrightarrow{R_{2}^{2}BH} \xrightarrow{R^{1}}_{H}C = C \xrightarrow{I}_{BR_{2}^{2}} \xrightarrow{R^{3}C \equiv CLi} \xrightarrow{R^{1}}_{H}C = C \xrightarrow{RR_{2}^{2}}_{C \equiv CR^{3}}$$
(1)

The conjugated enynyldialkylboranes have three functions, one carbon-carbon double bond, one carbon-carbon triple bond, and one boron-carbon bond combined to the double bond. This structural feature seems to promise a wide variety of their applications to organic syntheses. In this paper we wish to report cross-coupling reactions of the enynyldialkylboranes with allyl bromide or 1bromo-l-alkynes as one of examples of the synthetic use of these organoboranes.

We initially attempted a cross-coupling reaction of the enynyldialkylborane (<u>la</u>), prepared by the successive reactions of l-iodo-l-hexyne with bis(1,2-dimethylpropyl)borane and l-hexynyllithium. <u>la</u> was allowed to react with allyl bromide in the presence of aqueous potassium hydroxide and a catalytic amount of bis(acetylacetonato)copper (Eq. 2). A cross-coupling reaction proceeded under mild reaction conditions (room temperature, 24 h) and 6-(2-propenyl)-5-dodecen-7-yne (2a) was isolated from the worked-up reaction mixture by column chromatography (purity was above 99%) in 70% overall yield, starting from 1-iodo-1-hexyne, the precursor of 1a. A comparison of  $\delta$  value (5.82) of the alkenyl proton of 2a in <sup>1</sup>H NMR with that (5.55) of (<u>E</u>)-6-(2propenyl)-5-dodecen-7-yne (3), obtained by our previous work<sup>4</sup>) revealed that 2a had a Z configuration.

Similar cross-coupling reactions proceeded also in the case of more sterically hindered enynyldialkyboranes, derived from 3,3-dimethyl-1butynyllithium and 2-phenylethynyllithium giving corresponding regiospecifically substituted enynes, 2b and 2c, in similar yields.

A similar cross-coupling reaction of la with l-bromo-l-hexyne gave a conjugated endiyne, 7-(l-pentyliden)trideca-5,8-diyne ( $\frac{4a}{2a}$ ), in 45% overall yield, starting from l-iodo-l-hexyne.

Like in the cases of allyl bromide, corresponding conjugated endiynes,  $\frac{4}{20}$  and  $\frac{4}{20}$  were obtained from  $\frac{1}{20}$  and  $\frac{1}{20}$  respectively (Eq. 3).

$$1 \xrightarrow{n-C_{4}H_{9}C \equiv CBr}_{Cu(acac)_{2}/OH} \xrightarrow{n-C_{4}H_{9}}_{H}C = C_{C \equiv CR^{3}} \xrightarrow{La, 4a: R^{3}=n-C_{4}H_{9}}_{Lb, 4b: R^{3}=t-C_{4}H_{9}}$$

$$4 \xrightarrow{La, 4a: R^{3}=n-C_{4}H_{9}}_{Lb, 4b: R^{3}=t-C_{4}H_{9}}$$

$$1a, 4a: R^{3}=n-C_{4}H_{9}$$

$$1b, 4b: R^{3}=t-C_{4}H_{9}$$

$$1c, 4c: R^{3}=c_{6}H_{5}$$

$$(3)$$

At present, we have no clear evidence for the configuration of the alkenyl moiety of 4b and 4c. However, there has been found no exception of the stereochemistry in bis(acetylacetonato)copper-catalyzed cross-coupling reaction of alkenyldialkylboranes with alkynyl halides (retention of

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configuration).<sup>4,5)</sup> Thus  $4b_{\infty}$  and  $4c_{\infty}$  seem to have <u>E</u> configuration.

Yields of the products in the representative reactions are shown in Table 1.

n-C4H92 (2)		Poroducts and yields/% <sup>b)</sup>	
H'CECR <sup>3</sup>		n-C4H9 <sup>C=C</sup> , <sup>CH</sup> 2 <sup>=CHCH</sup> 2	<sup>n-C</sup> 4 <sup>H</sup> 9 <sub>C=C</sub> <sup>C≡CC</sup> 4 <sup>H</sup> 9 <sup>-n</sup>
R <sup>3</sup>	Bromides	H' C≡CR <sup>3</sup>	H <sup>C</sup> C≡CR <sup>3</sup>
n-C <sub>4</sub> H <sub>9</sub>	CH <sub>2</sub> =CHCH <sub>2</sub>	70	
t-C4H9	CH <sub>2</sub> =CHCH <sub>2</sub>	71	
C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> =CHCH <sub>2</sub>	61	
n-C <sub>4</sub> H <sub>9</sub>	n-C <sub>4</sub> H <sub>9</sub> C≡C		45
t-C <sub>4</sub> H <sub>9</sub>	n-C <sub>4</sub> H <sub>9</sub> C≡C		40
C <sub>6</sub> H <sub>5</sub>	n-C <sub>4</sub> H <sub>9</sub> C≡C		35

Table 1. Yields of substituted enynes

a) Prepared by successive reactions of 10 mmol of l-iodo-l-hexyne with
10 mmol of bis(l,2-dimethylpropyl)borane and 10 mmol of l-alkynyllithium.
b) Isolated by column chromatography using silica gel and based on l-iodo-l-hexyne (purities were over 99%).

Examinations of the 2a, 2b, 2c, 4a, 4b, and 4c by <sup>1</sup>H NMR spectra and by vapor phase chromatography using a glass capillary column revealed that they were isomerically pure, indicating that the cross-coupling reaction proceeded in a stereospecific manner.

Some works, in which the alkenyl group of organoboranes was combined with an allyl or 1-alkynyl group giving doubly unsaturated hydrocarbons, have already been reported.<sup>6-9)</sup> However, in the present reaction two unsaturated groups, one 1-alkynyl and one allyl groups or two 1-alkynyl groups, were introduced successively to the  $\alpha$ -carbon atom of the alkenyl group of organoboranes in a regio- and stereoselective manner. Thus, triply unsaturated compounds, which cannot easily be prepared by other methods, are synthesized by a simple procedure and in situ.

The following procedure for the synthesis of 2a is representative. To a THF solution of l-iodo-l-hexenylbis(l,2-dimethylpropyl)borane, prepared by hydroboration of 10 mmol of l-iodo-l-hexyne with a THF solution of 10 mmol of bis(1,2-dimethylpropyl)borane, 5 ml of hexamethyltriamide phosphate<sup>10)</sup> (at room temperature) and 10 mmol of hexynyllithium in hexane (at -78 °C) were added. After removal of the solvent, THF and hexane, under reduced pressure at 40 °C, 15 ml of dry THF (at 0 °C), 5 ml of aqueous 2 mol dm<sup>-3</sup> KOH (at 0 °C) and 0.5 mmol of Cu(acac)<sub>2</sub> (at -15 °C) were successively added, and then the solution was stirred at room temperature for 24 h. The residual organic boron compound was decomposed by alkaline hydrogen peroxide. 1.43 g (70%) of  $\frac{2}{2}$  was isolated from worked-up reaction mixture by column chromatography using silica gel column (eluted by hexane). Analytical data of 2a are as follows.  $n_D^{20}$ =1.4804; <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS)  $\delta$ =0.83-0.96 (m, 6H), 1.23-1.55 (m, 8H), 1.95-2.15 (m, 2H), 2.29 (t, J=6 Hz 2H), 2.87 (d, J=6 Hz, 2H), 4.95-5.15 (m, 2H), 5.82 (t, J=6 Hz, 1H), and 5.74-5.92 (m, 1H); IR (neat) 2200 (w), 995 (m), and 910 cm<sup>-1</sup> (m); MS (m/z)204 (M<sup>+</sup>).

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