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

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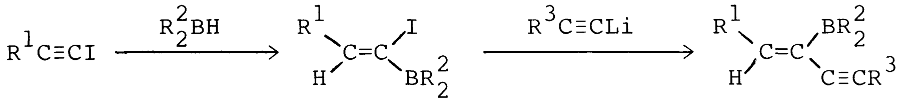
Internal enynyldialkylboranes give regio- and stereospecifically designed conjugated enynes, bearing an allyl or 1-alkynyl group on the internal alkenyl carbon atom, by a coupling reaction with allyl bromide or 1-bromo-1-alkynes.

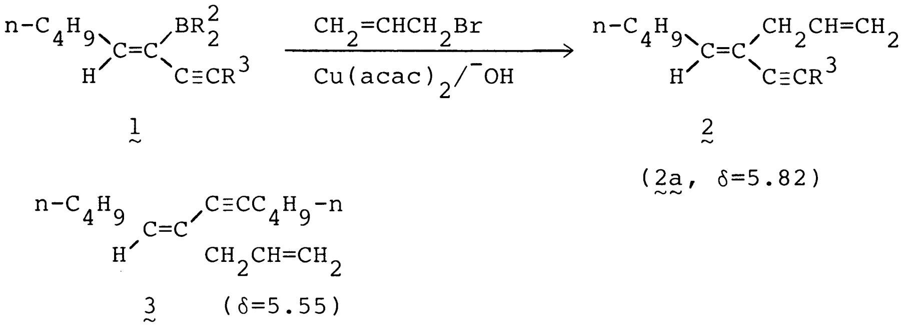
Although the chemistry of alkenylboranes has been developed, alkenylboranes appeared in most papers were confined to terminal ones.[1)] In relation to a synthesis of internal alkenylboranes,[2)] recently the authors synthesized conjugated enynyldialkylboranes by successive reactions of 1-iodo-1-alkynes with dialkylboranes and 1-alkynyllithiums(Eq. 1).[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 1-bromo-1-alkynes as one of examples of the synthetic use of these organoboranes.

We initially attempted a cross-coupling reaction of the enynyldialkylborane (**1a**), prepared by the successive reactions of 1-iodo-1-hexyne with bis(1,2-dimethylpropyl)borane and 1-hexynyllithium. **1a** 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 δ value (5.82) of the alkenyl proton of 2a in ^{1}H NMR with that (5.55) of (*E*)-6-(2-propenyl)-5-dodecen-7-yne (3), obtained by our previous work[4] revealed that 2a had a *Z* configuration.



1

2

(2a, δ=5.82)

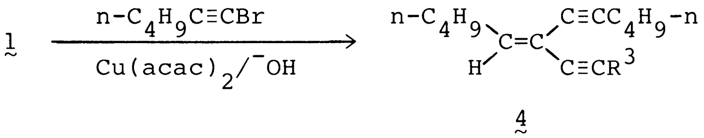
3 (δ=5.55)

1a, 2a: R^3=n-C_4H_9
1b, 2b: R^3=t-C_4H_9
1c, 2c: R^3=C_6H_5 (2)

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

A similar cross-coupling reaction of 1a with 1-bromo-1-hexyne gave a conjugated endiyne, 7-(1-pentyliden)trideca-5,8-diyne (4a), in 45% overall yield, starting from 1-iodo-1-hexyne.

Like in the cases of allyl bromide, corresponding conjugated endiynes, 4b and 4c were obtained from 1b and 1c respectively (Eq. 3).



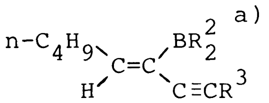
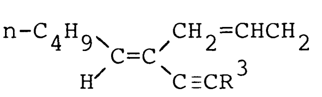
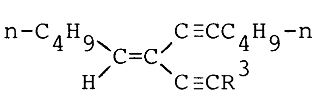
4

1a, 4a: R^3=n-C_4H_9
1b, 4b: R^3=t-C_4H_9
1c, 4c: R^3=C_6H_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 configuration).[4,5] Thus 4b and 4c seem to have E configuration.

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

Table 1. Yields of substituted enynes

 $n\text{-}C_4H_9(H)C{=}C(BR^2_2)C{\equiv}CR^3$ [a]		Poroducts and yields/%[b]	
R^3	Bromides	 $n\text{-}C_4H_9(H)C{=}C(CH_2{=}CHCH_2)C{\equiv}CR^3$	 $n\text{-}C_4H_9(H)C{=}C(C{\equiv}CC_4H_9\text{-}n)C{\equiv}CR^3$
$n\text{-}C_4H_9$	$CH_2{=}CHCH_2$	70	
$t\text{-}C_4H_9$	$CH_2{=}CHCH_2$	71	
C_6H_5	$CH_2{=}CHCH_2$	61	
$n\text{-}C_4H_9$	$n\text{-}C_4H_9C{\equiv}C$		45
$t\text{-}C_4H_9$	$n\text{-}C_4H_9C{\equiv}C$		40
C_6H_5	$n\text{-}C_4H_9C{\equiv}C$		35

a) Prepared by successive reactions of 10 mmol of 1-iodo-1-hexyne with 10 mmol of bis(1,2-dimethylpropyl)borane and 10 mmol of 1-alkynyllithium.
b) Isolated by column chromatography using silica gel and based on 1-iodo-1-hexyne (purities were over 99%).

Examinations of the 2a, 2b, 2c, 4a, 4b, and 4c by ^1H 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.[6-9] 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 α-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 1-iodo-1-hexenylbis(1,2-dimethylpropyl)borane, prepared by hydroboration of 10 mmol of 1-iodo-1-hexyne with a THF solution of 10 mmol of bis(1,2-dimethylpropyl)borane, 5 ml of hexamethyltriamide phosphate[10)] (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^{-3} KOH (at 0 °C) and 0.5 mmol of $Cu(acac)_2$ (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 **2a** 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; ^1H NMR ($CDCl_3$, TMS) δ=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^{-1} (m); MS (m/z)204 (M^+).

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10) An addition of hexamethyltriamide phosphate as co-solvent promotes the formation of the internal enynyldialkylboranes remarkablly.

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