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The Synthesis of Internal Conjugated (*E*)-Enynyldialkylboranes and Their Applications to the Syntheses of Conjugated Alkynones, Conjugated (*E*)-Enynes, and Conjugated Enynes Bearing an Unsaturated Group on the Double Bond

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Internal conjugated (*E*)-enynyldialkylboranes were synthesized by successive reactions of 1-iodo-1-alkynes with dialkylboranes and 1-alkynyllithiums in 31—79% yields. (*E*)-Enynyldialkylboranes, thus obtained, gave regio- and/or stereospecifically defined corresponding conjugated alkynones by alkaline hydrogen peroxide oxidation, conjugated (*E*)-enynes by protonolysis with acetic acid, and conjugated enynes bearing an unsaturated group on the internal alkenyl carbon atom by bis(acetylacetonato)copper-catalyzed cross-coupling reaction with allyl bromide or 1-bromo-1-hexyne respectively.

The authors recently investigated a cross-coupling reaction of 1-halo-1-alkenyldialkylboranes with alkylmagnesium halides. Regio- and stereospecifically designed internal (*E*)-alkenyldialkylboranes, thus obtained, could be utilized for regio- and stereospecific syntheses of ketones,[1] (*E*)-alkenes[1] and trisubstituted ethylenes[2] (Scheme 1).

An introduction of an alkynyl group to the α-carbon atom of alkenyldialkylboranes by a similar cross-coupling reaction was highly attractive because organoboranes which had an enyne structure on boron atom were expected to have a wide variety of applications as intermediates.

Zweifel *et al.* have previously reported a formation of internal (*Z*)-enynyldialkylboranes by a controlled hydroboration of conjugated diynes with dialkylborane.[3] However, in view of regioselectivity, this

$$R^1C{\equiv}C\text{-}C{\equiv}CR^2 \xrightarrow{R_2BH} R^1CH{=}C(BR_2)\text{-}C{\equiv}CR^2 + R^1C{\equiv}C\text{-}C(BR_2){=}CHR^2$$

reaction is applicable only to such diynes in which two alkyl groups are of the same structure with each other because of ambiguity of the site of hydroboration.

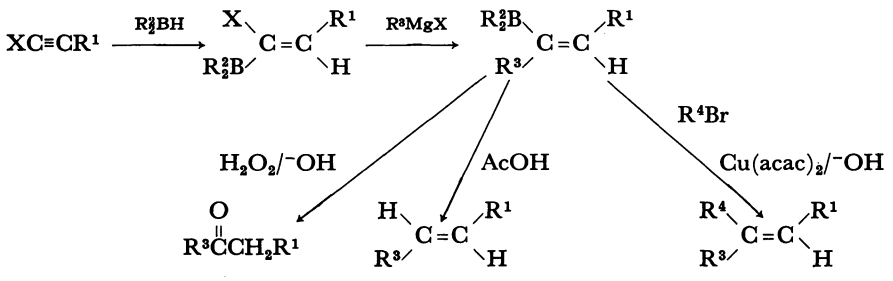
On the contrary, in internal enynyldialkylboranes, which might be obtained by our cross-coupling reaction, the situation of boron–carbon bond was clearly defined and both alkyl groups on the unsaturated bond could be chosen arbitrarily to a certain extent. In addition, the configuration of the alkenyl moiety was expected to be *E*.

Results and Discussion

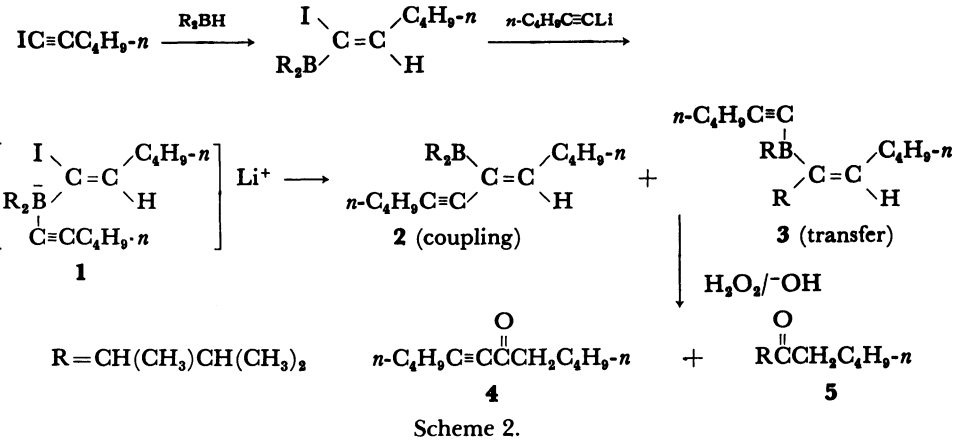
To find an appropriate procedure for the cross-coupling reaction, 1-bromo- or 1-iodo-1-hexyne was chosen as a starting material. It was hydroborated with dialkylborane and then treated with 1-hexynyl metal compound. As the hydroborating agent, dicyclohexylborane, bis(1,2-dimethylpropyl)borane and 9-borabicyclo[3.3.1]nonane (9-BBN) were examined, and as the 1-hexynyl metal compound, 1-hexynylmagnesium bromide and 1-hexynyllithium were examined respectively.

At the moment, we have no appropriate means to estimate the yield of the enynyldialkylborane (**2**), coupling product in Scheme 2, directly. However, it has been shown that alkenylboranes react readily with alkaline hydrogen peroxide to afford corresponding carbonyl derivatives.[4,5] Thus the yield of **2** was estimated from the amount of 7-dodecyn-6-one (**4a**) formed by alkaline hydrogen peroxide oxidation of the reaction mixture (Scheme 2).

In all cases examined, **4a** was formed in the yields ranging from 13% to 66%, based on the starting 1-halo-1-alkyne, indicating that **2** was formed at least in these yields. On the other hand, appreciable amount of cyclohexyl pentyl ketone or 2,3-dimethyl-4-nonanone (**5**) was formed in most cases, except for the case of 9-BBN, indicating that internal alkenyldialkylborane (**3**), whose one of the alkyl groups on the double bond was transfered from boron atom, (transfer product, in



Scheme 1.



Scheme 2.

Table 1. Yields of organoboranes obtained by the reactions of 1-halo-1-hexenyldialkylboranes with alkynyllithiums[a]

R^2[d]	X	$R^3C{\equiv}CLi$ (10 mmol) R^3	Solvent	Products and yields/%[c] $R^3C{\equiv}CCOC_5H_{11}$-n	$R^2COC_5H_{11}$-n[e]
c-C_6H_{11}	I	n-C_6H_{13}	THF	13	76
C_5H_{11}	I	n-C_6H_{13}	THF	60	14
C_5H_{11}	Br	n-C_4H_9	THF	43	33
C_5H_{11}	I	n-C_4H_9	THF	66	20
C_5H_{11}	I	n-C_4H_9	THF (30 ml) HMPT (5 ml)	79	7

a) The reactions were carried out in THF at −78 °C for 1 h. b) Prepared from 10 mmol of 1-halo-1-alkyne and 10 mmol of dialkylborane. c) Estimated from the amounts of ketones obtained by the alkaline hydrogen peroxide oxidation of the reaction mixture. d) C_5H_{11} is 1,2-dimethylpropyl. e) See Ref. 6.

Table 2. Yields of organoboranes obtained by the reactions of 1-iodo-1-alkenyl-bis(1,2-dimethylpropyl)boranes with alkynyllithiums[a]

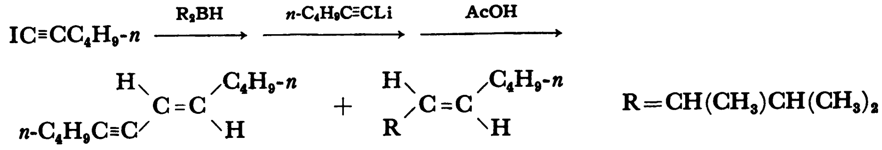
R^1	$R^3C{\equiv}CLi$ (10 mmol) R^3	Products and yields/%[c] $R^3C{\equiv}CCOCH_2R^1$	$R^2COCH_2R^1$[d]
n-C_4H_9	n-C_4H_9	(**4a**), 79	7
n-C_4H_9	t-C_4H_9	(**4b**), 70	5
n-C_4H_9	n-C_6H_{13}	(**4c**), 75	5
n-C_4H_9	C_6H_5	(**4d**), 31	14
n-C_6H_{13}	n-C_4H_9	(**4e**), 72	4

a) The reactions were carried out in 30 ml of THF and 5 ml of HMPT at −78 °C for 1 h. b) Prepared from 10 mmol of 1-iodo-1-alkyne and 10 mmol of bis(1,2-dimethylpropyl)borane. c) Estimated from the amounts of ketones (in the parentheses) obtained by the alkaline hydrogen peroxide oxidation of the reaction mixture. d) See Ref. 6.

Scheme 2), was also formed in the reaction.[6]

The best result was obtained when 1-iodo-1-hexyne was hydroborated with equimolar amount of bis(1,2-dimethylpropyl)borane in THF, and then treated with equimolar amount of 1-hexynyllithium in a mixture of hexane and THF, giving 66% yield of **4a** and 20% yield of **5** after the hydrogen peroxide oxidation. An addition of hexamethylphosphoric triamide (HMPT), as a co-solvent, showed a remarkable effect on the distribution of the products, increasing the amount of **4a** to 79% and decreasing the amount of **5** to 7%. Some of these results are shown in Table 1.

Coupling reactions of 1-iodo-1-alkenylbis(1,2-dimethylpropyl)boranes with some 1-alkynyllithiums



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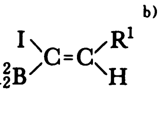
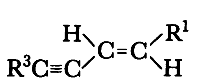
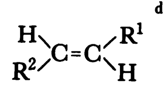
Scheme 3.

Table 3. Yields of alkenynes and alkenes obtained by the protonolyses of the internal enynylbis(1,2-dimethylpropyl)boranes[a)]

 b) R^1	$R^3C{\equiv}CLi$ (10 mmol) R^3	Products and yields/%[c)] 	 d)
n-C_4H_9	n-C_4H_9	**6a**, 76	7
n-C_4H_9	t-C_4H_9	**6b**, 69	5
n-C_4H_9	n-C_6H_{13}	**6c**, 70	5
n-C_4H_9	C_6H_5	**6d**, 50	19
n-C_6H_{13}	n-C_4H_9	**6e**, 68	5

a) The protonolyses were carried out using 10 ml of acetic acid at room temperature for 5 h. b) Prepared from 10 mmol of 1-iodo-1-alkyne and 10 mmol of bis(1,2-dimethylpropyl)borane. c) Determined by GLC. d) See Ref. 8.

were examined in the same manner as described above. These results are shown in Table 2.

Not only in the case of unbranched alkynyllithiums but also in the case of a branched one, 3,3-dimethyl-1-butynyllithium, desired enynyldialkylboranes were formed in fairly good yields. These results suggest that the present reaction is generally applicable to the introduction of alkynyl group on the α-alkenyl carbon atom of the alkenyldialkylboranes. (Phenylethynyl)-lithium also gave the desired product, though the yield was somewhat poor.

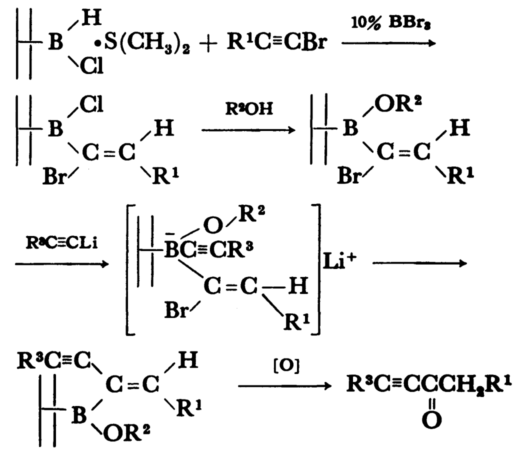
It has been shown that protonolysis of alkenylboranes with carboxylic acid provided corresponding alkenes in retention of configuration.[7)] Accordingly, protonolysis of the internal enynyldialkylboranes should provide corresponding enynes, and thus examinations of the structure of these enynes should reveal the configuration of the alkenyl moiety of the internal enynyldialkylboranes.

As expected, conjugated enynes were obtained by the protonolysis of the reaction mixtures. For example, the reaction mixture, obtained by the successive reactions of 1-iodo-1-hexyne with bis(1,2-dimethylpropyl)borane and 1-hexynyllithium, was protonolyzed with acetic acid giving 76% yield of (E)-5-dodecen-7-yne (**6a**) and 7% yield of (E)-2,3-dimethyl-4-nonene (**7**) respectively (Scheme 3).

Examinations of these enynes by GLC using a glass capillary column and by ^{1}H NMR spectra revealed that they were isomerically pure. The E configuration was assigned for all of them by their absorptions of the alkenyl proton in IR spectra, near 965 cm^{-1}, and in ^{1}H NMR spectra, coupling constant, about 16 Hz. Thus, it was revealed that the coupling reaction occured in a complete inversion of configuration giving internal (E)-enynyldialkylboranes (Scheme 2). In the protonolysis reactions, a small amount of (E)-alkenes,[8)] in which one of alkyl groups was transfered from the boron atom, was formed in nearly comparative yield to that of the corresponding alkanones appeared in Table 2. These results are shown in Table 3.

From the results shown in Tables 2 and 3, it is suggested that two reactions are involved in the present reaction. For example, both the coupling product **2** and the transfere product **3** are formed from borate complex (**1**) in a competitive manner.

The reactions, described above, are of interest as synthetic methods for conjugated alkynones and conjugated (E)-enynes using organoboranes. However, during the progress of our work, Brown *et al.* reported a synthesis of internal conjugated enynylborinic ester and its application to the synthesis of conjugated alkynones (61—63% yield).[9)]



However, the internal (E)-enynyldialkylboranes obtained by our reaction seemed to be potential inter-

mediates in organic synthesis. Thus, we continued our program to find new applications using these internal enynyldialkylboranes.

The authors previously found that a cross-coupling reactions of internal (*E*)-alkenyldialkylboranes, prepared by the reaction of 1-halo-1-alkenyldialkylboranes with alkylmagnesium halides, with allyl bromide or 1-bromo-1-alkynes was effectively catalyzed by bis(acetylacetonato)copper, giving (*E*)-1,4-dienes or conjugated (*E*)-enynes.[2] An application of this reaction to the present internal (*E*)-enynyldialkylboranes was expected to provide conjugated enynes having a third unsaturated carbon–carbon bond.

As expected, such triply unsaturated hydrocarbons were obtained in the reactions and some of these results have been communicated briefly.[10] However the authors wish to report more detailed experimental results of the reactions. Because the reactions were carried out by relatively simple procedure and *in situ*, giving dienynes or endiynes in highly regio- and/or stereospecific manner, and, thus, they seemed synthetically interesting.

Preliminary experiments using the reaction mixture of **2** and **3**, obtained as described above, with allyl bromide revealed that this cross-coupling reaction was affected appreciably by the reaction conditions, such as the reaction temperature, the amount of catalyst, and the kind and the amount of alkali metal hydroxide added as the aqueous solution. The best result was obtained when the reaction mixture was treated with equimolar amount of allyl bromide at −15 °C in the presence of 5 mole% of bis(acetylacetonato)copper and equimolar amount of aqueous potassium hydroxide (Scheme 4).

6-Allyl-5-dodecen-7-yne (**8a**) was isolated from the worked-up reaction mixture by column chromatography in 70% yield, based on starting 1-iodo-1-hexyne. A comparison of δ value (5.82) of the conjugated alkenyl proton of **8** in ^{1}H NMR with that (5.55) of (*E*)-6-allyl-5-dodecen-7-yne (**10**) obtained by our previous work,[2] revealed that the reaction proceeded in retention of configuration. Thus, **8a** has *Z* configuration.

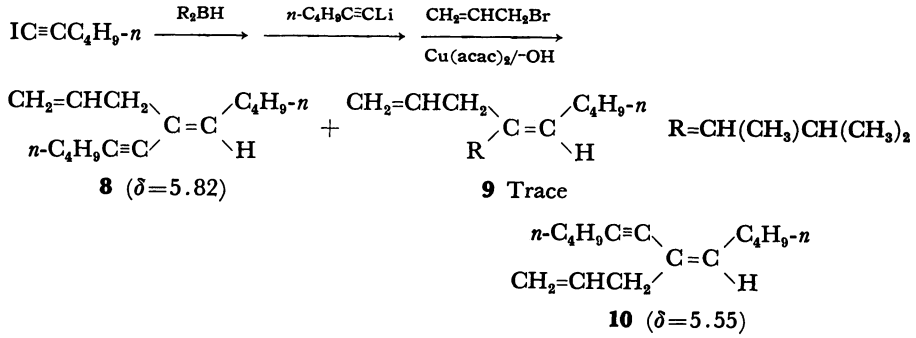
Similar results were also obtained with such (*E*)-enynyldialkylboranes, substituted by *t*-butyl or phenyl group at the triple bond, giving corresponding regio- and stereospecifically substituted enynes in fairly good yields.

A cross-coupling reaction of **2** with 1-bromo-1-hexyne was also carried out in similar reaction conditions (Scheme 5). In this case, aqueous sodium hydroxide was preferable to aqueous potassium hydroxide. 7-Pentylidene-5,8-tridecadiyne (**11a**) was formed almost uncontaminated by **12**. **11a** was isolated from the worked-up reaction mixture by column chromatography. Similar enediynes were obtained in the reactions of other internal (*E*)-enynyldialkylboranes with 1-bromo-1-alkynes.

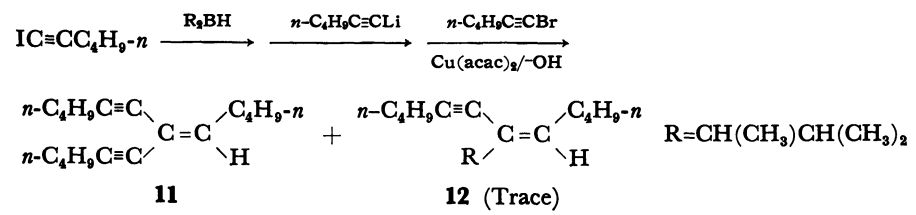
At present, we cannot reveal configurations of these enediynes from their spectral data or by direct comparisons with authentic samples. However, in bis(acetylacetonato)copper-catalyzed cross-coupling reactions of alkenyldialkylboranes with 1-halo-1-alkynes, 1-alkynyl groups were exclusively introduced to the α-carbon atom in retention of configuration.[2,11] Thus, these enediynes seem to be formed in retention of configuration.

These results are shown in Table 4.

Examinations of these triply unsaturated hydrocarbons by ^{1}H NMR and by GLC using a glass capillary column revealed that they were isomerically pure, indicating that the reaction proceeded in a stereospecific manner.



Scheme 4.



Scheme 5.

TABLE 4. YIELDS OF THE SUBSTITUTED ENYNES OBTAINED BY THE CROSS-COUPLING REACTIONS OF THE ENYNYBIS(1,2-DIMETHYLPROPYL)BORANES WITH ALLYL BROMIDE OR 1-BROMO-1-HEXYNE[a)]

$R^2_2B(R^3C{\equiv}C)C{=}C(R^1)H$ [b)]		Bromides	Products and yields/%[c)]	
R^1	R^3	(10 mmol)	$CH_2{=}CHCH_2(R^3C{\equiv}C)C{=}C(R^1)H$	$n\text{-}C_4H_9C{\equiv}C(R^3C{\equiv}C)C{=}C(R^1)H$
n-C_4H_9	n-C_4H_9	$CH_2{=}CHCH_2$	**8a**, 70	
n-C_4H_9	t-C_4H_9	$CH_2{=}CHCH_2$	**8b**, 71	
n-C_4H_9	n-C_6H_{13}	$CH_2{=}CHCH_2$	**8c**, 66	
n-C_4H_9	C_6H_5	$CH_2{=}CHCH_2$	**8d**, 61	
n-C_6H_{13}	n-C_4H_9	$CH_2{=}CHCH_2$	**8e**, 66	
n-C_4H_9	n-C_4H_9	n-$C_4H_9C{\equiv}C$		**11a**, 45
n-C_4H_9	t-C_4H_9	n-$C_4H_9C{\equiv}C$		**11b**, 40
n-C_4H_9	n-C_6H_{13}	n-$C_4H_9C{\equiv}C$		**11c**, 30
n-C_4H_9	C_6H_5	n-$C_4H_9C{\equiv}C$		**11d**, 35
n-C_6H_{13}	n-C_4H_9	n-$C_4H_9C{\equiv}C$		**11e**, 42

a) The reactions were carried out in the presence of alkaline $Cu(acac)_2$. b) Prepared by the successive reactions of 10 mmol of 1-iodo-1-alkyne with 10 mmol of bis(1,2-dimethylpropyl)borane and 10 mmol of 1-alkynyllithium. c) Isolated by column chromatography using silica gel and based on starting 1-iodo-1-alkyne.

As appeared in Table 2, the internal (E)-enynyldialkylboranes, obtained in the present reaction, were always contaminated by a certain amount of corresponding internal (E)-alkenyldialkylboranes, (transfer product). In the cross-coupling reactions with allyl bromide or 1-bromo-1-hexyne, these contaminants should also provide corresponding coupling products, because in our previous work, the internal (E)-alkenyldialkylboranes provided corresponding enynes under similar reaction conditions.[2)] However, fortunately, there have been detected only trace amount of such enynes in the present coupling reactions. For example, a mixture of about 7.9 mmol of **2** and 0.7 mmol of **3** provided 7 mmol of **8a** in the reaction with allyl bromide, and 4.9 mmol of **11a** in the reaction with 1-bromo-1-hexyne, almost uncontaminated by **9** and **12** respectively (Scheme 4 and Scheme 5).

These results may be attributed to the electronic character of the alkenyl moiety of organoboranes. That is, it is specurated that bis(acetylacetonato)copper can coordinate preferentially with the conjugated enynyl group on **2** to the enyl group on **3**, giving only the substituted enynes derived from **2**.

Some works, in which the alkenyl group of organoboranes were combined with the allyl or 1-alkynyl group giving doubly unsaturated hydrocarbons, have been reported.[2,11,13–15)] 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 regio- and stereospecific manners. Thus, triply unsaturated hydrocarbons, which cannot easily be obtained by other methods, are synthesized in the present reaction.

Experimental

Instruments. IR spectra (film) were recorded by using a Hitachi 285 spectrometer. ^1H and ^{13}C sectra ($CDCl_3$, TMS) were run on a JNM-FX200S spectrometer. Mass spectra were recorded by using a Hitachi M-52 mass spectrometer.

Reagents. 2-Methyl-2-butene and cyclohexene were dried over lithium aluminium hydride and distilled under argon stream. Commercial 1-hexyne, 1-octyne and phenylacetylene were dried over Molecular Sieve 4A. 3,3-dimethyl-1-butyne was prepared by the method described in the literature,[16)] and dried over Molecular Sieve 4A. 1-Iodo-1-hexyne,[17)] 1-iodo-1-octyne,[17)] and 1-bromo-1-hexyne[18)] were prepared by the method described in the literatures, and they were dried over Molecular Sieve 4A. Bis(1,2-dimethylpropyl)borane and dicyclohexylborane in THF were prepared as described in the literature.[19)] HMPT was distilled under argon stream after drying over calcium hydride and stored over Molecular Sieve 4A.

*Representative Procedures. The Synthesis of **2** and Its Hydrogen Peroxide Oxidation.* A 100-ml round-bottomed flask, equipped with a gas inlet for argon, a sample inlet with a serum cap and a magetic stirring bar, was flushed with argon. In the flask, 1-iodo-1-hexenylbis(1,2-dimethylpropyl)borane was prepared by the addition of 1.40 g of 2-methyl-2-butene (20 mmol) to BH_3 (10 mmol) in THF at −10 °C and the solution was stirred at 0 °C for 2 h. 2.08 g of 1-iodo-1-hexyne (10 mmol) was added slowly to the solution at −10 °C and the solution was stirred at 0 °C for 1 h, and then allowed to stand for additional 1 h to complete the reaction. Then 5 ml of anhydrous HMPT was added as the co-solvent and the solution was cooled to −78 °C immediately. To this solution, 1-hexynyllithium, prepared by the reaction of 0.82 g of 1-hexyne (10 mmol) in THF with butyllithium (10 mmol) in hexane, was added and the reaction mixture was maintained at −78 °C for 1 h. Then the solution was allowed to warm to room temperature and oxidized with alkaline hydrogen peroxide. The reaction mixture was extracted three times with diethyl ether, and the combined extracts were washed twice with NaCl-saturated water. Then it was dried over anhydrous magnesium sulfate. The solution was analyzed by GLC (5% FFAP, Diasolid M) using the internal standard method.

In the preparative reaction, the solvent was evaporated

off after the work-up and the residue was put on a column packed with silica gel (Wako gel Q-50). 1.3 g (72% yield) of 7-dodecyn-6-one, **4a**, was eluted with benzene. ^{1}H NMR δ=0.93 (t, J=7 Hz, 6H), 1.25—1.75 (m, 10H), 2.37 (t, J=7 Hz, 2H), and 2.52 (t, J=7 Hz, 2H);[20] ^{13}C NMR δ=13.50, 13.89, 18.63, 21.97, 22.40, 23.86, 29.75, 31.16, 45.51, 80.90 (C≡C), 94.21 (C≡C), and 188.62 (C=O); IR 2200 (C≡C) and 1680 (C=O) cm^{-1};[18] MS m/z 180 (M$^+$).

The Protonolysis of **2**. To the reaction mixture, obtained as described above, 10 ml of acetic acid was added at 0 °C, and the solution was stirred at room temperature for 5 h. 10 ml of water was added to the solution and the solution was extracted three times with hexane. The combined extracts were neutralized with aqueous sodium carbonate, washed twice with NaCl-saturated water and dried over anhydrous magnesium sulfate. The solution was analyzed by GLC (5% FFAP, Diasolid M) using the internal standard method. In the preparative reaction, the solvent was evaporated off after work-up and the residue was put on a column packed with silica gel (Wako gel Q-50). 1.1 g (76% yield) of (*E*)-5-dodecen-7-yne, **6a**, was isolated by elution with *n*-hexane. ^{1}H NMR δ=0.91 (m, 6H), 1.25—1.60 (m, 8H), 2.00—2.14 (m, 2H), 2.23—2.34 (m, 2H), 5.45 (dt, J=16 and 1.5 Hz, 1H), and 6.04 (dt, J=16 and 7 Hz, 1H);[21] ^{13}C NMR δ=13.65, 13.39, 19.07, 22.01, 22.18, 30.97 (2C), 32.67, 79.18 (C≡C), 88.64 (C≡C), 109.80 (-CH=) and 143.32 (-CH=); IR 2200 (C≡C) and 960 (⟩C=C⟨) cm^{-1};[19] MS m/z 164 (M$^+$).

The Cross-Coupling Reaction of **2** *with Allyl Bromide.* From the reaction mixture containing **2**, and **3**, obtained as described above, the solvents (THF and *n*-hexane) were removed under reduced pressure, and 10 ml of new THF was added. Then, 5 ml of aqueous 2 mol dm^{-3} solution of KOH was added at 0 °C and stirring was continued for 0.5 h at room temperature. The solution was cooled again to −15 °C, and 0.13 g of Cu(acac)$_2$ (0.5 mmol) was added under weak argon flow. Then the reaction mixture was warmed to room temperature, and stirring was maintained for 20 h. The solution was oxidized with alkaline hydrogen peroxide to decompose the residual organoboranes. The solution was extracted three times with diethyl ether. The combined extracts were washed twice with NaCl-saturated water and dried over anhydrous magnesium sulfate. The solvent was evaporated off and the residue was put on a column packed with silica gel (Wako gel Q-50). 1.43 g (70% yield) of (*Z*)-6-allyl-5-dodecen-7-yne, **8a**, was isolated by elution with *n*-hexane. ^{1}H NMR δ=0.91 (m, 6H), 1.25—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), 5.81 (t, J=7 Hz, 1H), and 5.75—5.90 (m, 1H); ^{13}C NMR δ=13.65, 13.94, 18.97, 21.97, 22.38, 27.92, 31.04, 31.45, 35.76, 82.39 (C≡C), 87.42 (C≡C), 115.42 (CH_2=), 120.87 (>C=), 135.51 (-CH=), and 137.27 (-CH=); IR 910 (CH_2=) cm^{-1}; MS m/z 204 (M$^+$).

The Cross-Coupling Reaction of **2** *with 1-Bromo-1-hexyne.* The reaction and the work-up procedures were the same as described above. 1.21 g (45% yield) of 7-pentylidene-5,8-tridecadiyne, **11a**, was isolated by elution with *n*-hexane. ^{1}H NMR δ=0.81—1.00 (m, 9H), 1.18—1.75 (m, 12H), 2.20—2.40 (m, 6H), and 6.14 (t, J=7 Hz, 1H); ^{13}C NMR δ=13.62, 13.87, 13.96, 19.00, 19.19, 21.97, 22.01, 22.33, 30.21, 30.33, 30.77 (2C), 76.72 (C≡C), 79.27 (C≡C), 86.84 (C≡C), 93.50 (C≡C), 105.81 (>C=), and 146.70 (-CH=); IR 2220 (C≡C) cm^{-1}; MS m/z 244 (M$^+$).

Analytical data of the other products are as follows.

*2,2-Dimethyl-3-decyn-5-one (**4b**)*: ^{1}H NMR δ=0.90 (t, J=7 Hz, 3H), 1.28 (s, 9H), 1.30—1.40 (m, 4H), 1.60—1.75 (m, 2H) and 2.51 (t, J=7 Hz, 2H); IR (film) 2210 (C≡C) and 1680 (C=O) cm^{-1}; MS m/z 180 (M$^+$).

*7-Tetradecyn-6-one (**4c**)*: ^{1}H NMR δ=0.90 (t, J=7 Hz, 6H), 1.25—1.75 (m, 14H), 2.36 (t, J=7 Hz, 2H), and 2.51 (t, J=7 Hz, 2H); IR 2200 (C≡C) and 1680 (C=O) cm^{-1}; MS m/z 208 (M$^+$).

*1-Phenyl-1-octyn-3-one (**4d**)*: ^{1}H NMR δ=0.91 (m, 3H), 1.25—1.40 (m, 4H), 1.65—1.80 (m, 2H), 2.64 (t, J=7 Hz, 2H), 7.35—7.45 (m, 3H), and 7.50—7.60 (m, 2H); IR 2190 (C≡C) and 1670 (C=O) cm^{-1}; MS m/z 200 (M$^+$).

*5-Tetradecyn-7-one (**4e**)*: ^{1}H NMR δ=0.93 (m, 6H), 1.25—1.75 (m, 14H), 2.37 (t, J=7 Hz, 2H), and 2.52 (t, J=7 Hz, 2H); IR 2210 (C≡C) and 1680 (C=O) cm^{-1}; MS m/z 208 (M$^+$).

*(E)-2,2-Dimethyl-5-decen-3-yne (**6b**)*: ^{1}H NMR δ=0.89 (t, J=7 Hz, 3H), 1.23 (s, 9H), 1.25—1.40 (m, 4H), 2.00—2.12 (m, 2H), 5.44 (dt, J=16 and 1.5 Hz, 1H), and 6.02 (dt, J=16 and 7 Hz, 1H); IR 2200 (C≡C) and 960 (⟩C=C⟨) cm^{-1}; MS m/z 164 (M$^+$).

*(E)-5-Tetradecen-7-yne (**6c**)*: ^{1}H NMR δ=0.89 (m, 6H), 1.25—1.60 (m, 12H), 2.00—2.15 (m, 2H), 2.20—2.35 (m, 2H), 5.44 (dt, J=16 and 1.5 Hz, 1H), and 6.03 (dt, J=16 and 7 Hz, 1H); IR 2220 (C≡C) and 960 (⟩C=C⟨) cm^{-1}; MS m/z 192 (M$^+$).

*(E)-1-Phenyl-3-octen-1-yne (**6d**)*: ^{1}H NMR δ=0.89 (t, J=7 Hz, 3H), 1.25—1.45 (m, 6H), 2.05—2.20 (m, 2H), 5.67 (dt, J=16 and 1.5 Hz, 1H), 6.22 (dt, J=16 and 7 Hz, 1H), 7.20—7.30 (m, 3H), and 7.35—7.45 (m, 2H); IR 2200 (C≡C) and 960 (⟩C=C⟨) cm^{-1}; MS m/z 184 (M$^+$).

*(E)-7-Tetradecen-5-yne (**6e**)*: ^{1}H NMR δ=0.91 (m, 6H), 1.20—1.60 (m, 12H), 2.00—2.10 (m, 2H), 2.20—2.35 (m, 2H), 5.44 (dt, J=16 and 1.5 Hz, 1H), and 6.03 (dt, J=16 and 7 Hz, 1H); IR 2210 (C≡C) and 960 (⟩C=C⟨) cm^{-1}; MS m/z 192 (M$^+$).

*(Z)-2,2-Dimethyl-5-allyl-5-dodecen-3-yne (**8a**)*: ^{1}H NMR δ=0.89 (m, 3H), 1.23 (s, 9H), 1.20—1.60 (m, 4H), 2.00—2.20 (m, 2H), 2.86 (d, J=6 Hz, 2H), 4.95—5.15 (m, 2H), 5.79 (t, J=7 Hz, 1H), and 5.70—5.95 (m, 1H); ^{13}C NMR δ=13.91, 22.38, 27.90, 30.87 (-C-), 31.21 (CH_3-, 3C), 31.45, 35.93, 80.71 (C≡C), 95.91 (C≡C), 115.32 (CH_2=), 120.92 (>C=), 135.56 (-CH=), and 136.75 (-CH=); IR 2220 (C≡C) and 910 (CH_2=) cm^{-1}; MS m/z 204 (M$^+$).

*(Z)-6-Allyl-5-tetradecen-7-yne (**8c**)*: ^{1}H NMR δ=0.89 (m, 6H), 1.20—1.60 (m, 12H), 2.00—2.15 (m, 2H), 2.28 (t, J=6 Hz, 2H), 2.87 (d, J=6 Hz, 2H), 4.95—5.20 (m, 2H), 5.81 (t, J=7 Hz, 1H), and 5.75—5.95 (m, 1H); ^{13}C NMR δ=13.94, 14.06, 19.31, 22.38, 22.60, 27.92, 28.56, 28.95, 31.40, 31.48, 35.76, 82.44 (C≡C), 87.50 (C≡C), 115.40 (CH_2=), 120.94 (>C=), 135.54 (-CH=), and 137.22 (-CH=); IR 910 (CH_2=) cm^{-1}; MS m/z 232 (M$^+$).

*(Z)-1-Phenyl-3-allyl-3-octen-1-yne (**8d**)*: ^{1}H NMR δ=0.91 (m, 3H), 1.20—1.60 (m, 4H), 2.05—2.25 (m, 2H), 2.98 (d, J=6 Hz, 2H), 4.95—5.25 (m, 2H), 5.75—6.15 (m, 1H), 6.03 (t, J=7 Hz, 1H), and 7.15—7.60 (m, 5H); ^{13}C NMR δ=13.94, 22.38, 28.14, 31.35, 35,47, 86.86 (C≡C), 91.56 (C≡C), 115.76 (CH_2=), 120.55 (>C=), 123.77 (>C=), 127.71 (-CH=), 128.19 (-CH=, 2C), 131.45 (-CH=, 2C), 135.22 (-CH=), and 139.30 (-CH=); IR 910 (CH_2=) cm^{-1}; MS m/z 224 (M$^+$).

*(Z)-7-Allyl-7-tetradecen-5-yne (**8e**)*: ^{1}H NMR δ=0.91 (m, 6H), 1.15—1.60 (m, 12H), 1.95—2.15 (m, 2H), 2.29 (t, J=6 Hz, 2H), 2.89 (d, J=6 Hz, 2H), 4.95—5.15 (m, 2H), 5.81 (t, J=7 Hz, 1H), and 5.70—5.95 (m, 1H); ^{13}C NMR δ=13.62, 14.08, 19.00, 21.97, 22.62, 28.22, 29.02, 29.29, 31.06, 31.72, 35.76, 82.41 (C≡C), 87.40 (C≡C), 115.37 (CH_2=), 120.89 (>C=), 135.51

(-CH=), and 137.27 (-CH=); IR 910 (CH_2=) cm^{-1}; MS *m/z* 232 (M^+).

(E)-6-(3,3-Dimethyl-1-butynyl)-5-tetradecen-7-yne (11b): ^1H NMR δ=0.90 (m, 6H), 1.23 (s, 9H), 1.20—1.55 (m, 8H), 2.20—2.40 (m, 4H), and 6.14 (t, *J*=7 Hz, 1H); IR 2220 (C≡C) cm^{-1}; MS *m/z* 244 (M^+).

(E)-6-(1-Hexynyl)-5-tetradecen-7-yne (11c): ^1H NMR δ=0.90 (m, 9H), 1.15—1.70 (m, 16H), 2.25—2.40 (m, 6H), and 6.14 (t, *J*=7 Hz, 1H); ^{13}C NMR δ=13.62, 13.89, 14.06, 19.00, 19.19, 19.31, 19.51, 21.97, 22.33, 22.57, 28.65, 30.21, 30.77, 31.38, 76.72 (C≡C), 79.27 (C≡C), 86.91 (C≡C), 93.48 (C≡C), 105.84 (>C=), and 146.68 (-CH=); IR 2220 (C≡C) cm^{-1}; MS *m/z* 272 (M^+).

(E)-6-(2-Phenylethynyl)-5-dodecen-7-yne (11d): ^1H NMR δ= 0.94 (m, 6H), 1.20—1.70 (m, 8H), 2.30—2.50 (m, 4H), 6.33 (t, *J*=7 Hz, 1H), and 7.20—7.55 (m, 5H); ^{13}C NMR δ=13.60, 13.87, 19.22, 21.97, 22.35, 30.41, 30.75 (2C), 76.09 (C≡C), 85.820 (C≡C), 88.25 (C≡C), 94.23 (C≡C), 105.79 (>C=), 123.25 (>C=), 128.02 (-CH=), 128.17 (-CH=, 2C), 131.57 (-CH=, 2C), and 148.26 (-CH=); IR 2200 (C≡C) cm^{-1}; MS *m/z* 264 (M^+).

7-Heptylidene-5,8-tridecadiyne (11e): ^1H NMR δ=0.91 (m, 9H), 1.10—1.65 (m, 16H), 2.10—2.55 (m, 6H), and 6.14 (t, *J*= 7 Hz, 1H); ^{13}C NMR δ=13.65 (2C), 14.11, 19.00, 19.22, 21.97, 22.01, 22.62, 28.65, 28.95, 30.53, 30.77 (2C), 31.67, 76.72 (C≡C), 79.25 (C≡C), 86.86 (C≡C), 93.50 (C≡C), 105.74 (>C=), and 146.83 (-CH=); IR 2220 (C≡C) cm^{-1}; MS *m/z* 272 (M^+).

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