New Procedure for Synthesis of 1,4-Dienes and Monoolefins via Methylcopper-Induced Cross-Coupling of Alkenylboranes with Organic Halides[1]

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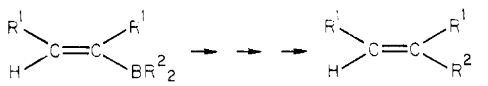
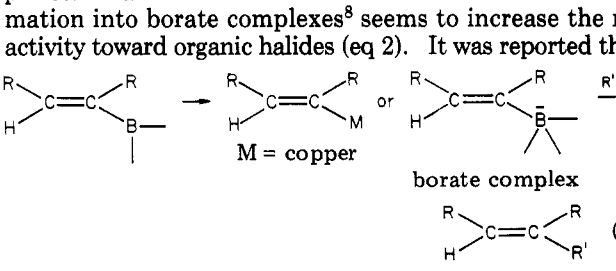
The treatment of dialkenylchloroboranes (**1**) with 3 equiv of methylcopper at −30 to ~−40 °C followed by addition of allylic halides gave 1,4-dienes. In the case of simple alkyl halides, the cross-coupling products were obtained with the aid of PhSLi or $P(OEt)_3$. A similar cross-coupling reaction of alkenyl-9-BBN (**13**) with allylic halides was realized by the use of 1 equiv of methylcopper, while cross-coupling with alkyl halides failed even in the presence of ligands. Systems such as dialkenylchloroborane–methylcopper and alkenyl-9-BBN–methylcopper reacted with substituted allylic halides predominantly at a γ position. The regioselectivity of the former system was quite simlar to that of the free alkenylcopper, while the regioselectivity of the latter system was greater than that of the free alkenylcopper. These results clearly indicate that the reactive intermediate of the latter system is an ate complex such as **19**.

In the past decade there has been wide interest in developing new methods to synthesize olefins in a stereoselective fashion. Total synthesis of polyunsaturated compounds,[2] particularly of fatty acids, with methylene-interrupted cis double bonds (1,4-diene structure) is frequently accompanied by synthesis of the corresponding polyacetylenic compounds, followed by partial catalytic hydrogenation. However, methylene-interrupted polyene compounds having trans and cis double bonds, such as insect pheromones,[3] cannot be constructed in this way. One of the possible approaches to the synthesis of a 1,4-diene system is cross-coupling of a vinylic organometallic[4] reagent with an allylic substrate. Such a cross-coupling is reported on an alkenylmercury,[5a] -alane,[8] -silane[5b], and -zirconium.[5c] Previously our group also reported a preliminary result on the cross-coupling via alkenylboranes.[1] This reaction is in marked contrast to the known olefin synthesis via alkenylboranes, which proceeds through an intramolecular migration procedure of R^2 from boron to carbon[6] (eq 1). Unfortunately, the migration procedure



(1)

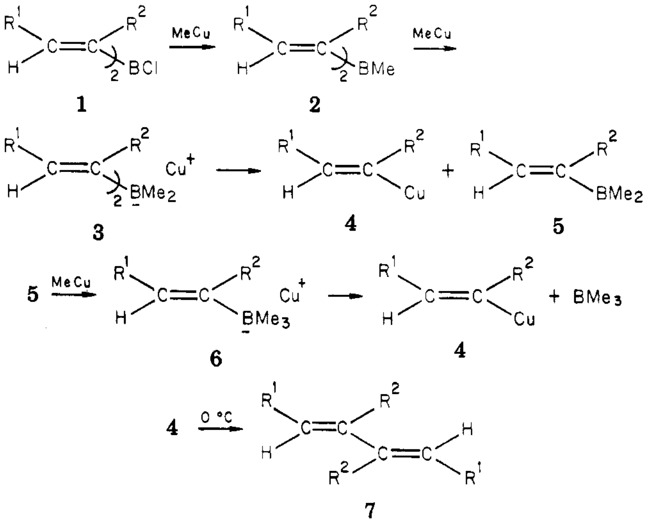
can only take place with a limited number of migrating groups. On the other hand, the direct coupling of alkenylboranes with organic halides appears to exclude such a limitation. The covalent nature of the B–C bond, however, sometimes makes it difficult to react with electrophiles. Transmetalation to other metals[1,5a,7] or transformation into borate complexes[8] seems to increase the reactivity toward organic halides (eq 2). It was reported that



(2)

the reaction of dialkenylchloroboranes (**1**) with 3 equiv of methylcopper gave the symmetrical 1,3-dienes (**7**) stereoselectively[7a] and that the reaction proceeded as shown in Scheme I.

Scheme I



This result suggests a possibility for the cross-coupling of alkenylboranes with organic halides. Indeed, the

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[1] For a preliminary report on some aspects of the present study, see Y. Yamamoto, H. Yatagai, A. Sonoda, and S-I. Murahashi, *J. Chem. Soc., Chem. Commun.*, 452 (1976).

[2] U. Axen, J. E. Pike, and W. P. Schneider, "Total Synthesis of Natural Products", J. Apsimon, Ed., Wiley, New York, p 81.

[3] C. A. Henrick, *Tetrahedron*, 1845 (1977).

[4] For a recent review see P. F. Hudrilik and A. M. Hudrilik, "The Chemistry of the Carbon–Carbon Triple Bond", Part I, S. Patai, Ed., Wiley, New York, p 199.

[5] (a) R. C. Larock, "New Application of Organometallic Reagents in Organic Synthesis", D. Seyferth, Ed., Elsevier, Amsterdam, p 257; (b) K. Tamao, J. Yoshida, M. Takahashi, H. Yamamoto, T. Kakui, H. Matsumoto, A. Kurita, and M. Kumada, *J. Am. Chem. Soc.*, **100**, 290 (1978); J. Yoshida, K. Tamao, A. Kurita, and M. Kumada, *Tetrahedron Lett.*, 1809 (1978); J. Yoshida, K. Tamao, M. Takahashi, and M. Kumada, *ibid.*, 2161 (1978); K. Tamao, T. Kakui, and M. Kumada, *ibid.*, 619 (1979); J. Yoshida, K. Tamao, T. Kakui, and M. Kumada, *ibid.*, 1141 (1979); K. Tamao, H. Mastumoto, T. Kakui, and M. Kumada, *ibid.*, 1137 (1979); (c) J. Schwartz and J. A. Labinger, *Angew. Chem., Int. Ed. Engl.*, **15**, 333 (1976); D. E. Van Horn and E. Negishi, *J. Am. Chem. Soc.*, **100**, 2252 (1978); E. Negishi, N. Okukado, A. O. King, D. Van Horn, and B. I. Spiegel, *ibid.*, **100**, 2254 (1978); N. Okukado, D. Van Horn, E. L. Klima, and E. Negishi, *Tetrahedron Lett.*, 1027 (1978).

[6] G. Zweifel, H. Arzoumanian, and C. C. Whitney, *J. Am. Chem. Soc.*, **89**, 3652 (1967); G. Zweifel, R. P. Fisher, J. T. Snow, and C. C. Whitney, *ibid.*, **94**, 6560 (1972); E. J. Corey and T. Ravindranathan, *ibid.*, **94**, 4013 (1972); G. Zweifel, R. P. Fisher, J. T. Snow, and C. C. Whitney, *ibid.*, **93**, 6309 (1971).

[7] For transmetalation to Cu see (a) Y. Yamamoto, H. Yatagai, and I. Moritani, *J. Am. Chem. Soc.*, **97**, 5606 (1975); (b) Y. Yamamoto, H. Yatagai, K. Maruyama, A. Sonoda, and S-I. Murahashi, *ibid.*, **99**, 5652 (1977). For transmetalation to Pd see (c) H. Yatagai, Y. Yamamoto, K. Maruyama, A. Sonoda, and S-I. Murahashi, *J. Chem. Soc., Chem. Commun.*, 852 (1977); H. Yatagai, Y. Yamamoto, and K. Maruyama, *ibid.*, 702 (1978); H. A. Dieck and R. F. Heck, *J. Org. Chem.*, **40**, 1083 (1975).

[8] E. Negishi, ref 5a, p 93.

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Table I. Methylcopper-Induced Cross-Coupling of 1 with Allylic Halides[a]

entry	alkyne	halide	product[b]	yield,[c] % (isolated)	regio-selectivity, γ:α
1	1-hexyne	allyl bromide	(*E*)-1,4-nonadiene (**10**)	95 (72)	
2	$Cl(CH_2)_3C{\equiv}CH$	allyl bromide	(*E*)-8-chloro-1,4-octadiene (**11**)	(48)	
3	5-decyne	allyl bromide	(*E*)-4-butyl-1,4-nonadiene (**12**)	58[d]	
4	1-hexyne	cinnamyl bromide	(*E*)-3-phenyl-1,4-nonadiene (**8a**) (*E*,*E*)-1-phenyl-1,4-nonadiene (**9a**)	(42)[e]	86:14
5	1-hexyne	crotyl chloride	(*E*)-3-methyl-1,4-nonadiene (**8b**) (*E*,*E*)-2,5-decadiene (**9b**)	50[f]	73:27

[a] Dialkenylchloroborane (10 mmol) was added to methylcopper (30 mmol) in ether at −30 to ∼−40 °C, and then the allylic halide was added. [b] Identified by IR, NMR, elemental analysis, and/or comparison with authentic materials. [c] By GLC analysis. The yields are based on the alkenyl group of **1**. [d] Symmetrical dimer was formed in 14% yield. [e] Total yield of **8a** and **9a**. [f] Total yield of **8b** and **9b**. Symmetrical dimer was formed in 50% yield.

Table II. Methylcopper-Induced Cross-Coupling of 13 with Allylic Halides[a]

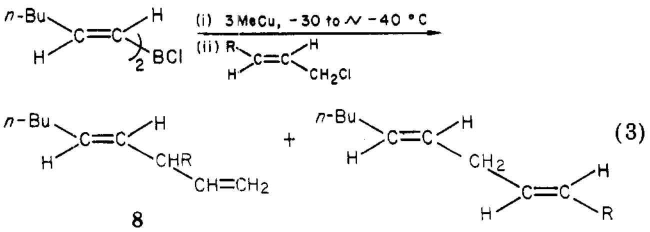
entry	alkyne	allylic halide	product[b]	yield,[c] %	regioselectivity, γ:α
1	1-octyne	crotyl chloride	(*E*)-3-methyl-1,4-undecadiene (**14**) (*E*,*E*)-2,5-dodecadiene (**15a**)	61	87.5:12.5
2	1-octyne	3-chloro-1-butene	**15a**,[d] (*Z*,*E*)-2,5-dodecadiene (**15b**)[d] **14**	60	87.5:12.5
3	1-octyne	cinnamyl chloride	(*E*)-3-phenyl-1,4-undecadiene (**16**) (*E*,*E*)-1-phenyl-undecadiene (**17**)	58	92:8

[a] Alkenyl-9-BBN (5 mmol) was added to methylcopper (5 mmol) in ether at 0 °C, and then the allylic halide was added. [b] Identified by IR, NMR, and elemental analysis. [c] Isolated yield based on alkenyl-9-BBN. [d] The ratio of **15a**/**15b** was 83:17, determined by GLC analysis using a golay column (squalene).

cross-coupling reaction was realized by the reaction of **1** with 3 equiv of methylcopper at low temperature followed by addition of the halide.[1] Full details of this cross-coupling reaction are reported here.

Results and Discussion

Methylcopper-Induced Cross-Coupling of 1 with Allylic Halides. In the mechanism given in Scheme I, alkenylcopper is involved as an intermediate. Since an alkenylcopper is stable at −30 to ∼−40 °C,[9] it appeared possible that treatment of **1** with 3 equiv of methylcopper at this temperature followed by addition of organic halides might suppress the formation of **7** and provide the cross-coupling product. Indeed this proved to be the case, and stereoselective synthesis of (4*E*)-1,4-dienes was realized by the methylcopper-induced cross-coupling of **1** with allylic halides. Similar reactions with crotyl and cinnamyl halides gave the γ-attack product **8** and α-attack product **9** in the ratio of 70:30 and 86:16, respectively (eq 3; see also Table I, entries 4 and 5). In the reaction of **1**, derived from the internal alkyne, dimerization competed with the desired cross-coupling reaction (cf. entries 3 and 5).



(3)

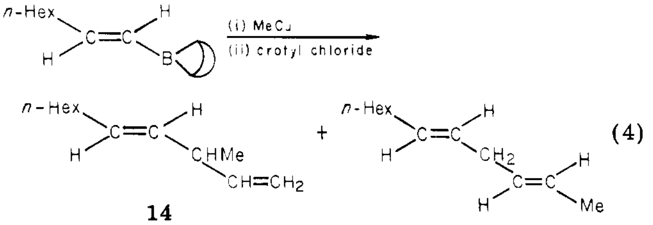
8
γ-attack product

9
α-attack product

a, R = Ph; b, R = Me

Methylcopper-Induced Cross-Coupling of Alkenyl-9-BBN (13)[10] with Allylic Halides. The reaction of alkenyldialkylboranes, such as alkenyldisiamylborane and alkenyl-9-BBN (**13**), with methylcopper was quite different from that of **1**. These alkenylboranes did not react with methylcopper at −30 °C, but did react at 0 °C. The reaction of alkenyldisiamylborane with methylcopper gave the dimer **7** even in the presence of allylic halides. In contrast, the reaction of alkenyl-9-BBN with 1 equiv of methylcopper immediately gave a dark green solution, and the subsequent addition of allylic halides gave the desired (4*E*)-1,4-dienes without the formation of dimers. The alkenylcopper intermediate from alkenyldisiamylborane may be too unstable, and may undergo competitive dimerization. The results are listed in Table II.

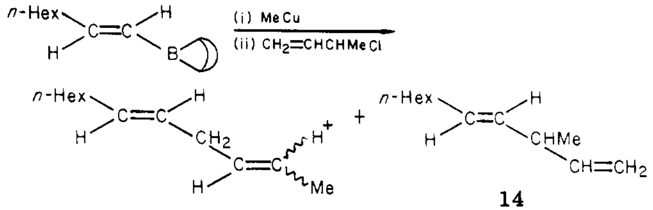
In this reaction, minor amounts of 1-olefin derived from unreacted alkenyl-9-BBN were obtained as a byproduct. This does not cause any difficulty in product isolation. The reactions with crotyl chloride and 3-chloro-1-butene are quite interesting, since both give predominantly γ-attack products (eq 4; see also Table II, entries 1, 2). This result suggested that the reaction did not proceed through



(4)

14
γ-attack product

15a
α-attack product



15a, 15b (cis isomer)
γ-attack product

14
α-attack product

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[9] G. M. Whitesides and C. P. Casey, *J. Am. Chem. Soc.*, **88**, 454 (1966); T. Kauffmann and W. Sahm, *Angew. Chem.*, **79**, 101 (1967).

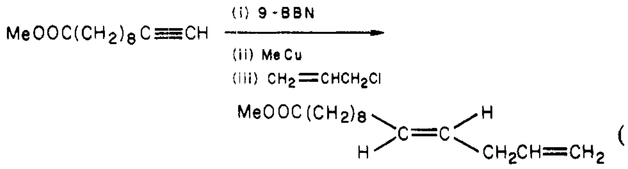
[10] H. C. Brown, C. G. Scouten, and R. Liotta, *J. Am. Chem. Soc.*, **101**, 96 (1979).

Table III. Cross-Coupling of Bis(1-hexenyl)chloroborane with Butyl Iodide in the Presence of Ligands[a]

ligand[b]	yield of (*E*)-5-decene,[c] %
$P(OPh)_3$	25
$P(n\text{-}Bu)_3$	26
$t\text{-}BuN{=}C$	37
PPh_3	47
$P(OEt)_3$	53

[a] Bis(1-hexenyl)chloroborane (1 mmol) was added to methylcopper (3 mmol) in ether at −30 to ∼−40 °C, and then ligand, HMPT, and BuI were added in that order. [b] Six equivalents of ligand was used. [c] GLC yields are based on the alkenyl group of the borane.

a common intermediate, such as an allyl cation or an allyl radical. α-Attack product, obtained by the reaction with crotyl chloride, retains the geometrical integrity of the original olefin (entry 1). A similar result was obtained in the reaction with cinnamyl chloride (entry 3). The alkyne-containing ester group, which cannot be hydroborated with chloroborane, could be converted to the (4*E*)-1,4-diene (**18**) by the method of eq 5. These results clearly indicate a synthetic usefulness of the present procedure.



(5)

18

Methylcopper-Induced Cross-Coupling Reaction of 1 with Alkyl Halides. In contrast to the cross-couplings with allylic halides those with simple alkyl halides were unsuccessful, presumably due to their low reactivities. Normant and co-workers succeeded in the cross-coupling of alkenylcoppers with alkyl halides by using ligands and HMPT as a cosolvent.[11] Accordingly, the cross-coupling of the alkenylcopper intermediate formed by the reaction of bis(1-hexenyl)chloroborane with 3 equiv of methylcopper with butyl iodide was performed in the presence of various ligands and HMPT as shown in Tables III and IV. The optimum yield of (*E*)-5-decene was obtained by using 6 equiv of triethyl phosphite. The use of triethyl phosphite, however, created a substantial difficulty in the product isolation. Instead, the use of 2 equiv of PhSLi as a ligand in DMF was more effective for the isolation of the product (eq 6). Presumably, the alkenylcopper intermediate can be associated with PhSLi to give the heterocuprate intermediate.[12] These results are given in Table V.

(6)

Unfortunately, the major disadvantage is that the reaction uses only one of the two alkenyl groups on boron. Alkenyldialkylborane having one alkenyl group, such as alkenyl-9-BBN, may provide the solution to this problem. However, the alkenylcopper intermediate obtained from alkenyl-9-BBN and 1 equiv of methylcopper did not react with alkyl halides, even in the presence of ligands. The reason is not clear, but it seems that this alkenylcopper intermediate may be strongly associated with the residual organoborane.

Table IV. Yield of (*E*)-5-Decene vs. Amounts of $P(OEt)_3$

$P(OEt)_3$, mmol	yield of decene, %
2	31
4	41
6	53
7	35
12	17
18	7

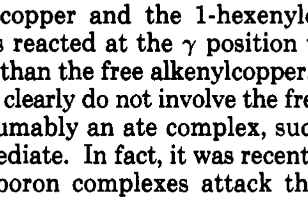
Table V. Methylcopper-Induced Cross-Coupling Reaction of 1 with Alkyl Halides[a]

alkyne	halide	ligand	product[b]	yield,[c] % (isolated)
1-hexyne	*n*-BuI	$P(OEt)_3$[d]	(*E*)-5-decene	53
1-hexyne	*n*-BuI	PhSLi[e]	(*E*)-5-decene[f]	(32)
1-hexyne	MeI	PPh_3	(*E*)-2-heptene	42
5-decyne	MeI	$P(OEt)_3$	(*Z*)-5-methyl-5-decene	25 (20)

[a] Dialkylenylchloroborane (10 mmol) was added to 3 equiv of methylcopper (30 mmol) in ether at −30 to ∼−40 °C, and then ligand, HMPT, and the alkyl halide were added in that order. [b] Identified by IR, NMR, and comparison with authentic materials. [c] GLC yield. The yields are based on the alkenyl group of 1. Major byproduct was symmetrical dimer. [d] Six equivalents of ligand was used. [e] Two equivalents of ligand was used. [f] Isolation was carried out with the aid of PhSLi.

Regioselectivity in the Reaction with Crotyl Chloride. The intermediate obtained via 1 is quite different from that via alkenyl-9-BBN (**13**) in the following ways: (1) in the reaction with allylic halides, the former gives the dimerization product as a byproduct, while the latter does not give such a dimer; (2) the former can be stabilized by the ligand and react with alkyl halide, while in the latter case such a ligand effect cannot be observed; (3) with substituted allylic halides, the regioselectivity (γ/α ratio) via the former intermediate is inferior to that via the latter intermediate (see Tables I and II).

The regioselectivity in the reaction of the alkenylcopper intermediates with crotyl chloride was investigated to clarify these differences (Table VI). The bis[(1-hexenyl)chloroborane]methylcopper and the free alkenylcopper systems exhibited similar regioselectivity, suggesting that the free alkenylcopper intermediate is involved in the former system. On the other hand, both the 1-octenyl-9-BBN–methylcopper and the 1-hexenylcopper–butyl-9-BBN systems reacted at the γ position with greater regioselectivity than the free alkenylcopper. Consequently, these systems clearly do not involve the free alkenylcopper instead, presumably an ate complex, such as **19**, is a reactive intermediate. In fact, it was recently reported that alkylcopper–boron complexes attack the γ position of allylic halides with greater regioselectivity than free alkylcoppers.[13]



19

Experimental Section

NMR spectra were recorded on JEOL JMN-MH-60 and JEOL PS-100 spectrometers; chemical shifts of compounds dissolved in CCl_4 are expressed in parts per million relative to Me_4Si. IR spectra were recorded on a Hitachi 215 spectrophotometer, and

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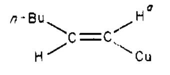
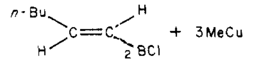
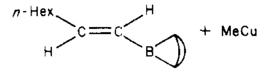
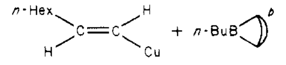
(11) J. F. Normant, G. Cahiez, and C. Chuit, *J. Organomet. Chem.*, **77**, 269 (1974).

(12) G. H. Posner, C. E. Whitten, and J. J. Sterling, *J. Am. Chem. Soc.*, **95**, 7788 (1973).

(13) K. Maruyama and Y. Yamamoto, *J. Am. Chem. Soc.*, **99**, 8068 (1977).

Table VI. Regioselectivity in the Reaction with Crotyl Chloride

reagent[c]	regio-selectivity, $\gamma:\alpha$
	77.5:22.5
	73:27
	87.5:12.5
	84:16

[a] Prepared from hexenyllithium and CuI at −30 to ∼−40 °C. [b] *n*-Bu-9-BBN was added to alkenylcopper at −30 °C. [c] In ether solvent.

GLC analyses were performed on a JEOL JGC-20K instrument using a 2-m column packed with SE-30 or silicone DC-550 on Celite 545 AW and a golay column coated with squalene or Apiezon. Elemental analyses were performed by the Microanalytical Laboratory of Kyoto University. High-resolution mass spectra were recorded on a JEOL JS-01-SG.

Reagent grade solvents were purified by standard techniques and kept over a drying reagent. $BH_3 \cdot THF$, $BH_2Cl \cdot OEt_2$, and 9-BBN were prepared by known methods.[19a] Methyllithium in ether was prepared by a standard procedure,[14] and butyllithium in hexane was a commercial product. Titrations were performed by the methods of Gilman[15] and Eastham.[16] Cuprous iodide was purchased and purified.[12] Hexyne, octyne, and 5-decyne were purchased. 5-Chloro-1-pentyne[17] and methyl 10-undecynoate[18] were prepared by known procedures.

Synthesis of 1,4-Dienes via Methylcopper-Induced Cross-Coupling of 1 with Allylic Halides. Dialkenylchloroboranes were prepared via hydroboration of alkynes[19] and were distilled under reduced pressure. In a 100-mL flask, equipped with a septum inlet and magnetic stirrer, was placed cuprous iodide (5.7 g, 30 mmol). The flask was flushed with argon and then maintained under a positive argon pressure. Dry ether (20 mL) was added and the flask was cooled to 0 °C with an ice bath. Methyllithium in ether (1.1 M, 30 mmol) was slowly added at 0 °C. The flask was then cooled to −30 to ∼−40 °C with a dry ice–H_2O–$CaCl_2$ bath. The dialkenylchloroborane (10 mmol) was slowly added. After the resulting mixture changed to a dark green solution, the allylic halide was added. The reaction mixture was allowed to warm to room temperature and became colorless. Water (30 mL) was added and the upper layer was separated. The precipitate which appeared in the water layer was filtered off and washed several times with ether. The combined ether solution was dried and concentrated. Distillation gave the desired product. Regioisomeric products were separated by preparative GLC. All new products exhibited the expected spectroscopic characteristics and provided satisfactory elemental analyses (Table VII).

Synthesis of 1,4-Dienes via Methylcopper-Induced Cross-Coupling of Alkenyl-9-BBN (13) with Allylic Halides. Alkenyl-9-BBN (13) was prepared according to the published procedure.[10] In a 50-mL flask, methylcopper (5 mmol) was prepared by the same procedure as above. Alkenyl-9-BBN (5 mmol) was added to this methylcopper solution at 0 °C. The color of the reaction mixture soon changed to dark green. After the mixture was stirred for 15 min, the allylic halide (5 mmol) was added. The resulting mixture was stirred overnight. Aqueous NH_4Cl (10 mL) was added and the upper layer was separated. The water layer was extracted several times with ether. The combined ether solution was concentrated, and the residue was chromatographed over alumina by using petroleum ether. Kugelrohr distillation gave the desired product. Regioisomers were separated by preparative GLC. In the case of methyl 10-undecynoate, the alkenyl-9-BBN was used directly after hydroboration, and the product was isolated by silica gel chromatography by using hexane as an eluant. All new products gave satisfactory ^1H NMR spectra and correct elemental analyses (Table VII).

Synthesis of Olefins via Methylcopper-Induced Cross-Coupling of 1 with Alkyl Halides. The dialkenylchloroborane (10 mmol) was added to methylcopper (30 mmol) in ether at −30 to ∼−40 °C. After the solution was stirred for 30 min, PhSLi (20 mmol) prepared from PhSH and BuLi in DMF (20 mL) was added. The resulting mixture was stirred for 5 min and alkyl halide (20 mmol) was added. The reaction mixture was allowed to warm to room temperature. Water (30 mL) was added and the mixture was extracted several times with ether. The combined ether solution was dried and concentrated. Distillation gave the desired product. The structure was identified by IR, ^1H NMR and mass spectroscopy and comparison with authentic materials. An authentic sample of 5-methyl-5-decene was prepared by a Wittig reaction.[20] This material contained cis and trans isomers in the ratio of 50:50. The other authentic materials are commercially available.

Isomeric Purity of 1,4-Dienes. An authentic sample of 12 was prepared according to Eisch's method:[21a] NMR (CCl_4) δ 5.64 (dd, J = 18, 10 Hz, 1 H), 5.00 (t, J = 6 Hz, 1 H), 4.98–4.76 (m, 2 H), 2.66 (d, J = 6 Hz, 2 H), 2.10–1.80 (m, 4 H) 1.52–1.08 (m, 8 H), 0.90 (t, J = 6 Hz, 6 H); IR 990, 910 cm^{-1}.

(*Z*)-4-Butyl-1,4-nonadiene, a stereoisomer of 12, was prepared by Zweifel's method.[21b] 5-Decyne (5 mmol) was hydroaluminated by $(i\text{-Bu})_2AlHMeLi$, prepared from $(i\text{-Bu})_2AlH$ and methyllithium, followed by addition of allyl bromide (10 mmol) in THF; the reaction mixture was refluxed for 2 h. After the addition of aqueous H_2SO_4(1 N), the resulting mixture was extracted several times with hexane. The hexane solution was washed with aqueous $NaHCO_3$ and saturated NaCl. Hexane was evaporated, and the residue was chromatographed over alumina by using petroleum ether. Kugelrohr distillation gave (*Z*)-4-butyl-1,4-nonadiene (40%): bp 140–160 °C (20 mmHg); NMR (CCl_4) δ 5.65 (dd, J = 10, 18 Hz, 1 H), 5.10 (t, J = 6 Hz, 1 H), 5.06–4.80 (m, 2 H), 2.73 (d, J = 6 Hz, 2 H), 2.16–1.80 (m, 4 H), 1.52–1.14 (m, 8 H), 0.88 (br t, J = 6 Hz, 6 H); IR 1630, 990, 905 cm^{-1}. Consequently, the *Z* and *E* isomers could be clearly distinguished by the chemical shift between 2.66 and 2.73 ppm; the NMR spectra of the reaction product completely accorded with that of the 4*E* isomer. Furthermore, these isomers could be separated by GLC (3 m, 30% Apiezon on Celite 545). The retention time of the 4*Z* isomer was shorter than that of the 4*E* isomer, and GLC analysis of the reaction product showed a single sharp peak with a retention time in accordance with that of the known 4*E* isomer. Accordingly, the reaction product was assigned to be 100% 4*E* isomer.

The stereochemistry of 2,5-dodecadiene (15), which consists of four stereoisomers, the 2*Z*,5*Z*, 2*E*,5*Z*, 2*Z*,5*E*, and 2*E*,5*E* isomers, was determined as follows. GLC examination using a golay column showed the α-attack product listed in Table II (entry 1) appeared as a sharp peak, and the NMR spectrum showed a single methyl signal adjacent to the double bond. The IR spectrum had a strong absorption at 965 cm^{-1}. These results show that the α-attack product is a single isomer; the 2*Z*,5*Z* isomer can be excluded because of the IR spectrum. Furthermore, the authentic sample of the 2*E*,5*Z* isomer[22] had a shorter retention time than the α-attack product. Accordingly, the α-attack product can be assigned to be either the 2*E*,5*Z* or the 2*E*,5*E* isomer. It should be

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[22] This material was prepared by cis reduction of (*E*)-dodec-2-en-5-yne.

Table VII. Properties of Olefinic Derivatives

compd	bp, °C (mmHg)	NMR, δ	IR, cm^{-1}	anal. or mass	
				found	calcd
11[a]	72-73 (20)	6.15-4.75 (m, 5 H), 3.48 (t, J = 6 Hz, 2 H), 2.73 (m, 2 H), 2.38-1.55 (m, 4 H)	1640 990 965 910	C, 66.15 H, 8.98 Cl, 24.72	C, 66.43 H, 9.06 Cl, 24.51
8a[a]	72-73 (20)	7.25 (m, 5 H), 6.33-4.83 (m, 5 H), 3.97 (m, 1 H), 2.03 (m, 2 H), 1.66 (m, 4 H), 0.93 (m, 3 H)	1640 1600 1500 965 910	C, 89.85 H, 10.03	C, 89.94 H, 10.06
9a[a]	72-73 (20)	7.50-7.17 (m, 5 H), 6.40-6.13 (m, 2 H), 5.66-5.43 (m, 2 H), 3.07-2.77 (m, 2 H), 2.23-1.83 (m, 2 H), 1.50-1.16 (m, 4 H), 0.92 (t, J = 6 Hz, 3 H)	1600 1500 965	C, 89.71 H, 10.08	C, 89.94 H, 10.06
8b[a]	80-90 (30)	6.50-5.83 (m, 1 H), 5.71-5.56 (m, 2 H), 5.40-5.00 (m, 2 H), 3.16-2.66 (m, 1 H), 2.16-1.83 (m, 2 H), 1.78-1.16 (m, 4 H), 1.10 (d, J = 7 Hz, 3 H), 0.93 (t, J = 6 Hz, 3 H)	1640 990 965 910	C, 86.60 H, 13.22	C, 86.88 H, 13.12
9b[a]	80-90 (30)	5.83-5.50 (m, 4 H), 2.90-2.63 (m, 2 H), 2.25-1.96 (m, 2 H), 1.83-1.66 (m, 3 H), 1.56-1.16 (m, 4 H), 0.93 (t, J = 6 Hz, 3 H)	965	C, 86.71 H, 13.10	C, 86.88 H, 13.12
14[b]	115-125 (20)	5.70 (ddd, J = 6, 10, 18 Hz, 1 H), 5.36-5.20 (m, 2 H), 4.88 (dd, J = 18, 2 Hz, 1 H), 2.88-2.64 (m, 1 H), 2.10-1.84 (m, 2 H), 1.44-1.20 (m, 8 H), 1.04 (d, J = 6 Hz, 3 H), 0.90 (t, J = 6 Hz, 3 H)	1640 965 990 910	C, 86.37 H, 13.33	C, 86.66 H, 13.34
15a[b]	125-130 (20)	5.40-5.28 (m, 4 H), 2.72-2.58 (m, 2 H), 2.02-1.94 (m, 2 H), 1.68-1.60 (m, 3 H), 1.36-1.24 (m, 8 H), 0.90 (t, J = 6 Hz, 3 H)	965	C, 86.63 H, 13.10	C, 86.66 H, 13.34
16[b]	100-110 (0.02)	7.34-7.04 (m, 5 H), 5.96 (ddd, J = 18, 10, 6 Hz, 1 H), 5.60-5.38 (m, 2 H), 5.04 (dd, J = 10, 2 Hz, 1 H), 4.96 (dd, J = 18, 2 Hz, 1 H), 3.92 (t, J = 6 Hz, 1 H), 2.16-1.92 (m, 2 H), 1.50-1.10 (m, 8 H), 0.90 (t, J = 6 Hz, 3 H)	1630 990 965 910	C, 89.33 H, 10.48	C, 89.41 H, 10.59
17[b]		7.30-7.10 (m, 5 H), 6.41-6.12 (m, 2 H), 5.68-5.40 (m, 2 H), 2.98-2.78 (m, 2 H), 2.12-1.80 (m, 2 H), 1.45-1.20 (m, 8 H), 0.90 (t, J = 6 Hz, 3 H)	1600 1500 965	M$^+$ 228.189 ± 0.005	M$^+$ 228.187792
18[b]		5.74 (ddd, J = 18, 10, 6 Hz, 1 H), 5.44-5.28 (m, 2 H), 4.94 (dd, J = 18, 2 Hz, 1 H), 4.88 (dd, J = 10, 2 Hz, 1 H), 3.60 (s, 3 H), 2.80-2.60 (m, 2 H), 2.20 (t, J = 6 Hz, 3 H), 2.10-1.84 (m, 2 H), 1.40-1.20 (m, 12 H)	1730 1640 990 965 910	M$^+$ 238.193 ± 0.005	M$^+$ 238.193269

[a] NMR spectrum run on 60-MHz instrument. [b] NMR spectrum run on 100-MHz instrument.

noted that the cross-coupling product retained the stereochemistry of the starting alkenylboranes. On the other hand, GLC examination revealed that the γ-attack product listed in Table II (entry 2) appeared as two peaks. The peak having shorter retention time corresponded to that of the α-attack product, and the ratio of retention times of the former to the latter was 83:17. The NMR spectrum of the γ-attack product showed two kinds of methyl signals adjacent to the double bond. Since the α-attack product (**15a**) of crotyl chloride consists of a single isomer and the γ-attack product of 3-chloro-1-butene consists of two isomers (**15a**) and (**15b**), it is reasonable to assign **15a** as the 2*E*,5*E* isomer.

Stereochemistry of Olefins. (*Z*)-5-Decene was prepared by cis reduction of 5-decyne;[23] (*E*)-5-decene was purchased. NMR spectra of (*E*)- and (*Z*)-5-decene irradiated at the methylene adjacent to the double bond showed singlets at 5.27 and 5.24 ppm, respectively. The irradiated spectra of the reaction product showed the singlet at 5.27 ppm and none of the signal 5.24 ppm was observed. Thus, isomeric purity was determined to 98%. The authentic sample of (*Z*)-5-methyl-5-decene,[20] which was an *E*/*Z* mixture, showed two peaks by GLC analysis using a golay column (Apiezon). The analysis of the reaction product under the same GLC conditions as above showed 98% isomeric purity. 2-Heptene was compared with commercially available material by the same method as above.

Regiochemistry. The reaction of hexenylcopper with crotyl chloride was performed as follows. Hexenyllithium was prepared from hexenyl iodide and butyllithium.[24] To a suspended solution of CuI (1 mmol) was added at −30 to ~−40 °C hexenyllithium. After the solution was stirred for 10 min, crotyl chloride (1 mmol) was added. Products were analyzed by GLC using dodecane as an internal standard.

Registry No. 8a, 60871-48-9; **8b**, 73062-32-5; **9a**, 73062-33-6; **9b**, 68712-23-2; **10**, 60835-96-3; **11**, 60835-97-4; **12**, 60835-98-5; **13**, 629-05-0; **14**, 73062-34-7; **15a**, 73062-35-8; **15b**, 73062-36-9; **16**, 73062-37-0; **17**, 73062-38-1; **18**, 73062-39-2; 5-chloropentyne, 14267-92-6; 5-decyne, 1942-46-7; allyl bromide, 106-95-6; (*E*)-cinnamyl bromide, 26146-77-0; (*E*)-crotyl chloride, 4894-61-5; 3-chloro-1-butene, 563-52-0; (*E*)-5-decene, 7433-56-9; 1-hexyne, 693-02-7; butyl iodide, 542-69-8; methyl iodide, 74-88-4; (*E*)-2-heptene, 14686-13-6; (*Z*)-5-methyl-5-decene, 20591-49-5; 5-decyne dimer, 73062-40-5; 1-hexyne dimer, 50284-89-4; (*Z*)-4-butyl-1,4-nonadiene, 73062-41-6; (*E*,*E*)-bis(2-hexenyl)chloroborane, 41929-38-8; (*E*)-9-(2-octenyl)-9-borabicyclo[3.3.1]nonane, 73062-42-7; [(*E*)-9-(10-methoxycarbonyl)-1-decenyl]-9-borabicyclo[3.3.1]nonane, 73062-43-8; (*E*)-cinnamyl chloride, 21087-29-6; 3-chloro-1-propene, 107-05-1; methylcopper, 1184-53-8; (*E*)-1-hexenylcopper, 54428-00-1; (*E*)-1-octenylcopper, 36661-57-1; 9-butyl-9-borabicyclo[3.3.1]nonane, 23532-74-3; P(OPh)$_3$, 101-02-0; P(*n*-Bu)$_3$, 998-40-3; *t*-BuNC, 7188-38-7; PPh$_3$, 603-35-0; P(OEt)$_3$, 122-52-1.

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(23) The reduction was preformed by using (*i*-Bu)$_2$AlH.

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