Novel and Convenient Method for the Stereo- and **Regiospecific Synthesis of Conjugated Alkadienes and** Alkenynes via the Palladium-Catalyzed Cross-Coupling Reaction of 1-Alkenylboranes with Bromoalkenes and Bromoalkynes¹

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Abstract: Details of a new and general method for the stereo- and regiospecific synthesis of conjugated alkadienes and alkenynes are described. The reaction of (Z)- or (Z)-1-alkenyldisiamylboranes, or 2-((E)-1-alkenyl)-1,3,2-benzodioxaboroles readily obtainable by hydroboration, with either (E)- or (Z)-1-alkenyl bromides in the presence of a catalytic amount of tetrakis-(triphenylphosphine) palladium and bases such as sodium alkoxides gives the corresponding (E,E)-, (E,Z)-, (Z,E)-, or (Z,E)-Z)-conjugated alkadienes stereo- and regiospecifically, while retaining the configurations of both the starting alkenylboranes and bromoalkenes. The reaction of (E)- and (Z)-1-alkenyldisiamylboranes with 1-bromoalkynes similarly provides a stereoand regiospecific synthesis of conjugated (E)- and (Z)-alkenynes. A mechanism of this cross-coupling reaction, which involves the transmetalation between a 1-alkenylborane and an alkoxypalladium(II) complex generated through the metathetical displacement of a halogen atom from RPd^{II}X with sodium alkoxide, is proposed.

The stereo- and regiospecific synthesis of conjugated alkadienes are of great importance in organic chemistry in themselves, as well as in their utilization in other reactions such as the Diels-Alder reaction. A number of new methods for the preparation of conjugated dienes and polyenes have been recently developed utilizing organometallic compounds, magnesium,² aluminum,³ boron,⁴ silicon,⁵ copper,^{6,7} silver,⁷ mercury,⁸ and zirconium⁹ reagents. For example, a highly stereoselective method for preparing (Z,Z) unsymmetrical dienes was first reported by Zweifel.^{4b} Those for preparing (E,E)- and (E,Z)-dienes using organoboranes were first reported by Negishi.^{4c,54} Although these methods have their own excellence, the scope of many of these reactions has still been limited by the nature of the organometallic involved or the procedure employed. For instance, some of the methods cited can only be applicable for the synthesis of symmetrical dienes,⁴⁻⁸ or because of the highly reducing property of the organometallic

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compounds (e.g., aluminum), the method³ can be used only for the synthesis of unfunctionalized dienes, or, in some cases, stoichiometric amounts of transition-metal catalysts are necessary.^{6,7}

Among these procedures, the most promising ones of preparing conjugated dienes or enynes in a stereospecific manner are perhaps those based on the direct cross-coupling reaction of stereodefined alkenylmetallics with stereodefined haloalkenes or haloalkynes with the aid of a catalytic amount of transition-metal catalysts.^{2,3,9} On the other hand, it is well-known that stereodefined 1-alkenyldiorganoboranes are readily prepared by the monohydroboration of alkynes; e.g., diorganoboranes such as disiamylborane and catecholborane permit the monohydroboration of terminal alkynes, thus making readily available the corresponding (E)-1alkenyldiorganoboranes (3) with high stereoselectivity, more than 99% (eq 1).^{10,11} Highly pure (Z)-1-alkenyldiorganoboranes (5)







5 · 6
$$\longrightarrow$$
 $H \xrightarrow{H}_{R^{2}}_{R^{2}}$ (4)

(purity, more than 98%) are prepared without any difficulty via the monohydroboration of 1-halo-1-alkynes with disiamylborane or dicyclohexylborane, followed by treatment with tert-butyllithium

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Table I. Cross-Coupling of (E)-1-Hexenylborane (9a or 9b) with (E)- β -Styryl Bromide (eq 5)^a

					yield (%) ^a of		of
9	catalyst ^b	base (equiv) ^c	solvent	reaction time, h	diene 11	PhCH=CH ₂ , 13	BuCH=CH(Sia),
	(THE	ــــــــــــــــــــــــــــــــــــــ			
L	$PuL_4(3)$	none	hanna	6	0		
D	$PaL_4(3)$	none	benzene	D	0		_
a	$PdL_4(3)$	2 M NaOMe(2)–MeOH	THF	2	59	4	5
а	PdL₄ (3)	2 M NaOEt(2)-EtOH	THF	2	73	1	2
а	$PdL_4(3)$	2 M NaOH (2) -H ₂ O	THF	2	59	0	5
b	$PdL_4(1)$	2 M NaOEt(2)-EtOH	THF	2	44	2	
Ь	$PdL_4(3)$	2 M NaOEt(2)-EtOH	THF	4	78	3	
b	$PdL_4(1)$	2 M NaOMe(2)-MeOH	benzene	2	61	3	
b	$PdL_4(1)$	2 M NaOEt(2)-EtOH	benzene	2	86	3	
b	$PdL_4(1)$	2 M NaOPh(2)-MeOH	benzene	2	73	1	
b	$PdL_4(1)$	2 M NaOH (2)-H ₂ O	benzene	2	86	0	
b	$PdL_4(1)$	2 M KOAc (2)– H_2O	benzene	2	27	1	
b	$PdL_4(1)$	Et_3N (5)	benzene	5	4	0	
b	$PdCl_2 \cdot L_2(1)$	2 M NaOEt(2)-EtOH	benzene	2	86	0	
b	$Pd(OAc)_2(1)$	2 M NaOEt(2)-EtOH	benzene	2	10 ^e	0	

^{*a*} All the reactions were conducted at boiling temperature of the solvent using 10% excess of **9b** or 50% excess of **9a**. ^{*b*}L is triphenylphosphine and in parenthesis the amount of the catalyst used is shown in mol % per styryl bromide. ^{*c*} Equivalents per styryl bromide. ^{*d*}Determined by GLC, based on (E)- β -styryl bromide by using an internal standard. ^{*c*} 2-Butyl-4-phenyl-1,3-butadiene (18%) was an accompanying product.

(eq 2).¹² Consequently, if such 1-alkenyldiorganoboranes react with 1-alkenyl halides or 1-alkynyl halides stereo- and regioselectivity, these reactions provide direct and convenient synthetic procedures for stereodefined conjugated alkadienes (eq 3 and 4) or alkenynes. In spite of the efforts by many workers to find such cross-coupling reactions, there were no successful reports^{3a,13} when we started the work.

At the initial stage of our exploration, we considered that the reason of difficulty in the coupling seemed to be based on the following feature. The common mechanism of transitionmetal-catalyzed cross-coupling reactions¹⁴ between organometallic compounds and organic halides involves sequential (a) oxidative addition, (b) transmetalation, and (c) reductive elimination. One of the major reasons why 1-alkenylboranes cannot react with 1-alkenyl or 1-alkynyl halides appears to be step (b), namely the transmetalation process between R'MX (M = transition metal; X = halogen) and organoboranes does not occur readily, because of the weak carbanion character of organic groups in the organoboranes. Therefore, if the organoborates formed from 1-alkenylboranes and basic species such as alkoxide, acetate, and hydroxide ions are used instead of alkenylboranes themselves, there may be a possibility that the transmetalation takes place more readily. Actually, we found that the reaction proceeds smoothly in the presence of bases to give the expected conjugated alkadienes and alkenynes stereo- and regiospecifically in excellent yields.

In this paper, we describe details of such a new versatile method for the stereo- and regiospecific synthesis of alkadienes and alkenynes, which we have already reported in form of short communications.¹

Results and Discussion

Synthesis of (E,E)-Alkadienes. When we attempted to carry out the coupling reaction of (E)- β -styryl bromide (10) with (E)-hexenyldisiamylborane (9a), prepared by the hydroboration of 1-hexyne with disiamylborane, in the presence of tetrakis-(triphenylphosphine)palladium, it failed to obtain the expected diene in any noticeable amount and the starting styryl bromide was recovered (Table I), as Negishi and Baba previously reported.^{3a} although they described an interesting stereospecific alkenyl-alkenyl cross-coupling by a palladium- or nickel-catalyzed reaction of alkenylalanes with alkenyl halides. However, we found that the addition of bases to the mixture brings dramatically about a rapid and clean coupling reaction. The optimum conditions for the synthesis of (E,E)-alkadienes were examined by the crosscoupling between (E)-1-hexenylborane (9a and 9b) and (E)- β styryl bromide (10) (eq 5), the results of which are summarized in Table I. In the parentheses of eq 5, the minor products obtained in small amounts are revealed.

Table I shows that high yields of the dienes are obtained when relatively strong bases such as sodium alkoxide, phenoxide, and hydroxide are used, whereas weak bases as sodium acetate and triethylamine are not effective in attaining high yields of the cross-coupling products. Although the solvent appears not to play

a critical role in determining the yields of the cross-coupling products in these reactions, a comparison of benzene and THF as the solvent under various conditions demonstrated that the higher yields of the dienes are yielded in a benzene solution. The yields of the dienes in the coupling in THF can be improved when the reactions are carried out for a longer period with an increasing amount of the catalyst. All the palladium complexes examined were found to be effective, but those having triphenylphosphine as a ligand were recognized to be most effective and to give the (E,E)-diene with high stereoselectivity, generally exceeding 98%. When palladium(II) acetate was employed as the catalyst, a substantial amount (18%) of 2-butyl-4-phenyl-1,3-butadiene,¹⁵ a product due to the head-to-tail cross-coupling was obtained as the byproduct. A comparison of disiamylborane (2a) and 1,3,2-benzodioxaborole (2b), which were used as the hydroborating reagents under various conditions, indicated that the higher yields of the dienes 11 can be obtained by the use of the latter. Although the use of disiamylborane results in the formation of an accompanying byproduct, e.g., 2,3-dimethyl-4-nonene (12) in some cases, the hydroboration with this borane can be carried out under milder conditions with high selectivity.¹⁰

In Table II are summarized the results of the cross-coupling between a variety of (E)-1-alkenylboranes and (E)-1-bromoalkenes. It is apparent from the table that alkenylboranes derived from terminal alkynes and those derived from internal alkynes give excellent yields of the expected conjugated dienes with high stereo- and regioselectivity. The isomeric purity of all the 1,3dienes exceeded 98%.

Thus, the above experiments showed that the conjugated (E,E)-dienes can be synthesized under mild conditions with high

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Table II. Synthesis of (E,E)-Dienes^a (Equation 3)

1-Alkenylborane 3b	1-Bromoalkene 4	Product	Yield(§) ^{<u>b</u> of diene}	lsomeric purity(%)
~~~~B<	Br	Ph	86	98
~~~~ ^{B&lt;}	Ph Br	Ph	80	100
~~~~B<	Br	$\sim\sim\sim$	81	100
Ph B<	Br	Ph	56	100
~~~~B<	Br	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	86	98
Ph B <	Br	Ph	78	99
B<	Br	Ph	93	100

^aAll reactions were carried out in benzene containing 2 equiv of NaOEt and 1 mol % of Pd(PPh₃)₄ at 80 °C for 2 h, using 10% excess of 3b. ^bGLC analysis based on 1-bromoalkenes.

yields and with high stereo- and regioselectivity by the present method.

Synthesis of (E,Z)- and (Z,Z)-Alkadienes. The (E)- and (Z)-1-alkenylboranes^{10,12} can easily be obtained via the hydroboration of appropriate alkynes or 1-haloalkynes. We examined the reactions of (E)- and (Z)-1-hexenylboranes with (E)- or (Z)- β -styryl bromide as coupling partners in order to check the utility of the present coupling reaction for the synthesis of (E,Z)- and (Z,Z)-dienes. Thus, when (Z)-1-hexenyldisiamylborane (14) and (Z)- β -styryl bromide (15) in benzene containing 2 equiv of sodium ethoxide in ethanol and 3 mol % of Pd(Ph₃)₄ were heated under reflux for 2 h, (1Z,3Z)-1-phenyl-1,3-octadiene (16) was formed in a 42% yield as the major product with the accompanying three isomers (1E,3E)-11 (1% yield), (1E,3Z)-17 (1%), and (1Z,3E)-diene 18 (2%). All such byproducts are shown in parentheses in eq 6.

The similar cross-coupling reaction of (Z)-1-hexenyldisiamylborane (14) with (E)- β -styryl bromide (10) under the conditions described above gave (1E,3Z)-diene 17 (49%) almost exclusively with a small amount of 11 (2%) (eq 7). The cross-

coupling of (E)-1-hexenyl-1,3,2-benzodioxaborole (9b) with (Z)- β -styryl bromide under similar conditions to the above gave

(1Z,3E)-1-phenyl-1,3-octadiene (18) in an 86% yield together with a 1% yield of the (E,E)-diene (eq 8).

These results clearly indicate that this palladium-catalyzed alkenyl-alkenyl cross-coupling reaction proceeds smoothly under the reaction conditions analogous to the synthesis of (E,E)-dienes to give the corresponding (E,Z)- and (Z,Z)-dienes while retaining the original configuration of both the starting alkenylboranes and the haloalkenes. Versatility of the synthesis of (E,Z)- and (Z,Z)-dienes has then been examined with a variety of 1-alkenylboranes and 1-bromoalkenes, and the results are summarized in Table III.

The (E,Z)-dienes can be synthesized either by the coupling reaction between (Z)-1-bromoalkenes and (E)-1-alkenyl-1,3,2benzodioxaboroles (**3b**) or by the coupling of (E)-1-bromoalkenes with (Z)-1-alkenyldisiamylboranes (**5**). The usefulness of the present method is illustrated by the stereospecific synthesis of (1Z,3E)-1-phenyl-4-cyclohexenyl-1,3-butadiene (**20**) (eq 9) and (3Z)-2-phenyl-1,3-octadiene (**22**) (eq 10). Thus, the triple bond



of 1-ethynylcyclohexene was selectively hydroborated with 1,3,2-benzodioxaborole to give 1,3,2-benzodioxaborole (19). Its cross-coupling with (Z)- β -styryl bromide (15) gave (1Z,3E)-1-phenyl-4-cyclohexenyl-1,3-butadienes (20) in an 87% yield with the isomeric purity of 98%. Synthesis of (3Z)-2-phenyl-1,3-octadiene (22) by the coupling reaction between (Z)-1-hexenyl-disiamylborane (14) and α -bromostyrene (21) is an example which shows that even thermally unstable dienes can be synthesized by

Table III. Synthesis of (E,Z)- and (Z,Z)-Dienes by the Cross-Coupling Reactions^a (equations 3 and 4)

1-Alkenylborane 3b or 5	1-Bromoalkene 6	Product	Yield(%) ^b of diene	lsomeric purity(%)	
BX2	Br Ph	Ph	86	98	
BX ₂	Br Ph		49	99	
BX ₂	Br	Ph Ph	42	89 ^e	
<u><u></u> BX2</u>	Br		88	98	
BX ₂	Br		49	98	
Ph BX ₂	Br Ph	Ph	89	98	
General Strategy Stra	Br Ph	Ph	8 7	98	
BX ₂	Br Ph	Ph	55	99	

^a The reactions were carried out in benzene containing 2 equiv of NaOEt in EtOH at 80 °C for 2 h, using 10% excess of 3b and 1 mol % of Pd(PPh₃)₄ or 30% excess of 5 and 3 mol % of Pd(PPh₃)₄. ^bGLC yield based on the bromoalkene employed. ^cX₂ = 1,3,2-Benzodioxaboryl. ^dX₂ = (3-methyl-2-butyl)₂. ^eThis low value of isomeric purity is due to the isomerization of (Z)- β -styryl bromide during the reaction.

the present method performed under mild conditions. The diene **22** is known to undergo a [1,5]-sigmatropic shift of a hydrogen atom quite readily,¹⁶ as we in fact confirmed its isomerization to 2-phenyl-2,4-octadiene (**23**) in an 88% yield on heating at 200 °C for 1 h (eq 10).

The coupling reaction with (E)-1-alkenyl-1,3,2-benzodioxaboroles always gives the dienes in ca. 90% yields while the coupling reaction with (Z)-1-alkenyldisiamylboranes gives less than 50% yields of the corresponding dienes. Nevertheless, (Z)-1-alkenylboranes are readily prepard only as (Z)-1-alkenyldisiamylboranes by the hydroboration of 1-haloalkynes with disiamylborane, followed by treatment with *tert*-butyllithium in good yields with high stereospecificity (>99%), without isolation and purification. Of course, (E,Z)-alkadienes are obtained by the cross-coupling reaction between (E)-1-alkenyl-1,3,2-benzodioxaboroles and (Z)-haloalkenes. In such cases, however, (Z)-haloalkenes are difficult to prepare in a stereodefined manner and are liable to isomerization during purification.

Table III also indicates that the (Z,Z)-dienes can be synthesized by the coupling reaction of (Z)-bromoalkenes with (Z)-1-alkenyldisiamylboranes in ca. 50% yields with high isomeric purity.

Synthesis of (E)- and (Z)-Alkenynes. The ready coupling of alkenylboranes with haloalkenes described above encouraged us to examine the extention of this method for the cross-coupling of alkenylboranes with haloalkynes, although a highly selective

synthesis of conjugated enynes by the Pd-catalyzed reaction of alkynylzinc reagents with alkenyl halides was previously reported.^{54b} It was found that unlike the alkenyl-alkenyl crosscoupling, 1-alkenyl-1,3,2-benzodioxaboroles were quite inert to haloalkynes, and all the attempts to obtain the cross-coupling enynes were unsuccessful. We found, however, that in contrast to alkenyl-1,3,2-benzodioxaboroles, 1-alkenyldisiamylboranes react with haloalkynes to give such cross-coupling enynes. Thus, the reflux of a benzene solution of (E)-1-hexenyldisiamylboranes (9a) and 1-bromooctyne (24) for 2 h in the presence of 1.4 equiv of a base and 1 mol % of Pd(PPh₃)₄ gave (5E)-tetradecen-7-yne (25) in a 98% yield with an isomeric purity of 99% (eq 11). The results are summarized in Table IV.

As observed in the case of the cross-coupling reaction of alkenylboranes and haloalkenes, the alkenyl-alkynyl coupling requies an only catalytic amount of $Pd(PPh_3)_4$ and a base such as sodium hydroxide and alkoxides. Although the cross-coupling products

$$g_a \rightarrow BrC \equiv CHex$$
 Bu $C \equiv CHex$ (11)
24 25

are obtained in very high yields in almost all the reactions, the combination of sodium methoxide as a base and benzene as a solvent gave a high turnover of the catalyst. The yields of the enynes were generally lower when less than 5 mol% of the catalyst was used in a THF solution. THF, however, can most conveniently be used as the solvent when alkenyldisiamylboranes are usually prepared. Chloroalkynes such as 1-chlorooctyne did not react with the both alkenylboranes (3 or 5) under the above conditions. The

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 Table IV. Cross-Coupling of (E)-1-Hexenylboranes with

 1-Bromooctyne^a (Equation 11)

9	base	solvent	catalyst ^c (mol %)	yield (%) ^b of enyne
b	1 M NaOMe in MeOH	benzene	$PdL_4(5)$	0
a	1 M NaOMe in MeOH	THF	$PdL_4(5)$	97
a	1 M NaOEt in EtOH	THF	$PdL_4(5)$	66
a	1 M NaOH in H ₂ O	THF	$PdL_4(5)$	86
a	1 M NaOMe in MeOH	benzene	$PdL_4(1)$	98

^{*a*}All the reactions were conducted at refluxing temperature of the solvent for 2 h, using 1.4 equiv of a base and 10% excess of 9. ^{*b*}Determined by GLC based on 1-bromooctyne. ^{*c*}L is PPh₃.

coupling reaction is highly regio- and stereoselective. The reaction of (Z)-1-hexenyldisiamylborane (14) with 1-bromooctyne was thus found to yield (5Z)-5-tetradecen-7-yne (26) in a 50% yield with an accompanying (5E) isomer (25) in an only 2.6% yield (eq 12).

$$14 \cdot Br C \equiv CHex \qquad \longrightarrow \qquad Bu \qquad (\cdot 25) \qquad (12)$$

The assigned (Z) configuration of 26 was confirmed by the magnitude (J = 11 Hz) of the coupling constant of the olefinic protons in the ¹H NMR spectrum and by the absence of a band at 955 cm⁻¹ due to the out-of-plane C-H bending vibration of the trans structure in the IR spectrum. The results including those from the reactions of several alkenylboranes with a variety of haloalkynes are summarized in Table V.

Mechanism of the Coupling Reaction. The principal features of the present cross-coupling reaction, which are important for delineating the mechanism, are as follows. (a) Only catalytic amounts of palladium complexes $(1 \sim 3 \mod \%)$ are required to obtain the cross-coupling products. (b) The coupling reactions are highly regio- and stereospecific and take place while retaining the original configurations of both the starting alkenylboranes and the haloalkenes. The isomeric purity of the products generally exceeds 97%. (c) A base is required to carry out a successful coupling. The related examination on the effect of bases indicated that two types of the product, one cross-coupled by a head-to-head and another cross-coupled by a heat-to-tail, can be obtained de-

RX = alkenyl, aryl, and allylic halides R' = alkyl and H.



Figure 1. Catalytic cycle for the coupling reaction of haloalkenes and haloalkynes with alkenylboranes.

pending on the kinds of bases. When we use hydroxide and alkoxides as bases, normal products arising from head-to-head coupling are exclusively obtained, whereas the use of Lewis bases such as triethylamine leads almost exclusively to head-to-tail cross-coupling products.¹⁵ On the role of bases, we considered at the initial stage of the investigation to increase the carbanion character of the alkenyl groups in organoboranes by their coordination with the boron atoms, thereby facilitating the transfer of alkenyl groups from the boron to the palladium complexes in the transmetalation step. In order to check this possibility, lithium (1-hexenylmethyl)disiamylborate (29) was examined to react with (E)- β -styryl bromide (10) in the presence of the coupling product

$$\begin{array}{ccc} & Me & & \\ B_{\mathbf{b}}(Sia)_{2} & \cdot & 10 & \xrightarrow{PdL_{4}} & Bu & & \\ & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & &$$

11, however, was found to be only 9%. This evidence indicates that the base does not function in such a way in the coupling reaction. (d) In some cases, small amounts of the reduction products (5%) arising from the starting haloalkenes were detected

Table V. Synthesis of (E)- and (Z)-Enynes by the Cross-Coupling Reactions^a

1-Alkenylborane 3a or 7	Bromoalkyne	Product	Yield(%) ^b of enyne	lsomeric purity(%)
B (Sia) ₂	BrC≡C		98	99
B(Sia) ₂	BrC≡C-Ph	~~~~ Ph	74	99
Ph B(Sia) ₂	BrC≡C	Ph	95	99
B(Sia) ₂	BrC≡C-Ph	Ph	93	96
B(Sia) ₂	BrC≡C		53 ^c	95

^a All reactions were carried out in benzene at the refluxing temperature for 2 h, using 1 mol % of Pd(PPh₃)₄, 1.4 equiv of MaOMe, and 10% excess of **3a** under nitrogen, unless otherwise noted. ^bGLC yield based on the bromoalkyne employed. ^c20% excess of the alkenylborane and 3 mol % of the catalyst were used.

Table VI. Reaction of 1-Hexenyl-1,3,2-benzodioxaborole (9b), with Allylic Phenoxides, Acetate, and Chlorides (Equation 15)^a

RCH=CH	ICH₂Y	
R =	Y =	yield (%) of diene 28
Н	OPh	75 ^b
Ph	OPh	64 ^c
Ph	OAc	12 ^c
Ph or H	Cl	$0^{b,c}$

^aReactions were carried out in benzene at the refluxing temperature for 4 h using 5 mol % of Pd(PPh₁)₄ and 10% excess of 1-hexenyl-1,3,2-benzodioxaborole (9b). b1,4-Nonadiene. c1-Phenyl-1,4-nonadiene.

(Table I). The formation of such reduction products may be attributable to the alkoxopalladium(II) intermediate formed by metathetical displacement, as shown in eq 14.^{17,18} (e) Allylic

$$RPdX \cdot L_n \rightarrow NaOMe \xrightarrow{-X^*} RPdOMe \cdot L_n \xrightarrow{-CH_1O} RPdH \cdot L_n$$
(14)

RH ٠ Pd L

phenoxides or acetates (27) were found to react with 1-hexenyl-1,3,2-benzodioxaborole (9b) in the absence of bases to give the corresponding coupling products (eq 15, Table VI). Such

$$9b \cdot Y \longrightarrow R \xrightarrow{PdL_4} Bu \longrightarrow R$$
 (15)
27 28

results should suggest that $(\pi$ -allylphenoxo)-¹⁹ and $(\pi$ -allylacetoxo)palladium(II) complexes generated via oxidative addition of allylic components to the palladium(0) complex readily react with alkenylboranes. (f) In order to confirm the possibility if alkoxopalladium(II) complexes are real intermediates in the catalytic cycles, the following reactions of 1-octenylboranes (30) were examined with various π -allylpalladium(II)²⁰ (31) (eq 16) and (trichlorovinyl)palladium(II) complexes (33)²¹ possessing different types of ligands (eq 17). The results are summarized in Table VII.

The results clearly indicate that the reaction takes place at room temperature when the complexes bearing Pd-O bonds are used, whereas the cross-coupling reaction does not proceed smoothly with the Pd-Cl complexes. The order of reactivity of the com-



plexes was MeO > acac and OAc \gg C1. The similar order on the effect of the ligands for the transmetalation between organoboranes and mercury(II) salts has been reported.²² Thus, all the above results can be reconciled with the involvement of an alkoxopalladium(II) complex as an intermediate in this coupling reaction.

The mechanism of the present cross-coupling reaction between alkenylboranes and organic halides catalyzed by palladium com-

plexes as well as bases, which accommodates all the above features of the reaction, is outlined in Figure 1. Like other related reactions which are catalyzed by transition metals,^{14a,18,23} especially by nickel, palladium, or rhodium, this coupling reaction should involve an oxidative addition²⁴ of organic halides to the palladium(0) complex (step a). This step is followed by the metathetical displacement of the halide ion from $RPdXL_2$ (A) to give an alkoxopalladium(II) or hydroxopalladium(II) complex (B)^{17,21} (step b). Such a Pd complex then reacts with an alkenylborane to provide the diorganopalladium complex (C) (step c). Finally, reductive elimination of the intermediate C yields the corresponding crosscoupling product and regenerates the catalyst (step d).

As it has been confirmed that in a number of related coupling reactions the steps a and d proceed through retention of configuration,^{2,3,9,23} the transmetalation between alkenylboranes and alkoxo- or hydroxopalladium(II) complexes (B) (step c) in the present reaction is also considered to take place via retention of configuration. In agreement with this, we recently found that the carboalkoxylation of alkenylboranes in the presence of palladium catalysts and bases proceeds in the similar manner with retention of configuration.25

These 1-alkenylboranes readily react not only with vinylic and acetylenic halides, as described in this paper, but also with a variety of organic halides such as aryl halides,²⁶ allylic and benzylic halides,²⁷ and 3,4-epoxy-1-butene²⁸ in the presence of catalytic amounts of palladium catalysts and 2 equiv of bases to give the desired cross-coupling products. Unsaturated carboxylic esters (α,β) are synthesized by the palladium-catalyzed carbonylation of 1-alkenylboranes.²⁵ The coupling of (2-ethoxyvinyl)boranes with aryl and benzyl halides provides a convenient method for the conversion of organic halides into aldehydes with two more carbon atoms.²⁹ The same type of reaction between arylboronic acids and haloarenes gives the corresponding cross-coupling products biaryls in good yields.30

Most recently, the versatility of the present method has been amply demonstrated by the stereospecific synthesis of natural products bearing conjugated alkadiene or alkenyne structures, e.g., sex pheromones, 31,32 trans-(C₁₀)allofarnesene, 33 bombykol and its three geometrical isomers, 34 and humulene, 35 Such reports have been recently reviewed.36

Conclusion

The palladium-catalyzed cross-coupling reaction of haloalkenes and haloalkynes with 1-alkenyldisiamylboranes or 1-alkenyl-1,3,2-benzodioxaboroles in the presence of bases such as sodium alkoxides has been demonstrated to proceed readily and stereoand regiospecifically to give conjugated alkadienes or alkenynes in high yields. The configurations of both the haloalkenes and

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Table VII. Reaction of 1-Octenylboranes (30) with π -Allylpalladium(II) or (Trichlorovinyl)palladium(II) Complexes (Equations 16 and 17)^a

ь

		Yield $(x)^{-}$ of the product $(32 \text{ or } 34)$ via the reaction with			
Pd - Complex	Reaction time, h	Hex B(Sia) ₂	Hex		
(Pd C1 /2	1	0	0		
χ	20	10	6		
Pd OAc /2	1	0	43		
<pre> Pd(acac) </pre>	1	7	37		
N N	5	23	45		
CI CI CI CI	16	0	0		
CI CI CI CI), 1	54	79		

^aAll the reactions were carried out in THF at room temperature under a nitrogen atmosphere. ^bGLC yield based on the Pd complex.

1-alkenylboranes are retained during the reaction, thus providing versatile and reliable procedures for the syntheses of stereodefined conjugated (E,E)-, (E,Z)-, (Z,E)-, and (Z,Z)-alkadienes and envnes under mild conditions.

The intermediacy of alkoxopalladium complexes in the proposed catalytic cycle has been shown by several experiments.

Experimental Section

All the experiments were carried out under a nitrogen atmosphere. 1-Hexyne, 1-octyne, 3-hexyne, phenylethyne, and methylethyne were used after distillation of the commercial reagents. 1-Cyclohexenylethyne was prepared according to the method reported by Brandsma.^{37,38} Diborane in THF and 1,3,2-benzodioxaborole were prepared by the known procedures.^{10,39} Benzene and THF were purified by distillation from benzophenone ketyl under a nitrogen atmosphere before use. The IR and ¹H NMR spectra were taken on a Hitachi-Perkin-Elmer Model 125 spectrophotometer and a Hitachi R-22 spectrometer at 90 MHz using Me₄Si as the internal reference, respectively. Mass spectra were recorded on a JEOL JMS-D 300. GLC analyses were performed with a Hitachi 163 gas chromatograph using a 2 m \times 3 mm column (15% SE-30 on Uniport B). GLC yields were determined using suitable hydrocarbon internal standards.

Alkenylboranes (3a and 3b). (E)-1-Alkenyldisiamylboranes (3a) were prepared via the hydroboration of appropriate acetylenes with disiamylborane-THF¹⁰ and were used without further purification. They were standardized by oxidation with alkaline hydrogen peroxide to be changed to corresponding alcohols. (E)-1-Alkenyl-1,3,2-benzodioxaboroles (**3b**) were prepared from 1,3,2-benzodioxaborole and alkynes according to the Brown's method^{10,38,40} in the yields of over 90% in all the cases. They were purified by distillation before use: $3b (R^1 = Bu$, $R^2 = H$) bp 86-87 °C (0.3 torr) [lit.⁴⁰ 82 °C (0.25 torr)]; 3b ($R^1 = Hex$, $R^2 = H$) bp 112–120 °C (0.2 torr); **3b** ($R^1 = Et$, $R^2 = Et$) bp 63 °C (0.1 torr) [lit.⁴⁰ 81 °C (0.2 torr)]; **3b** ($R^1 = Ph$, $R^2 = H$) bp 156 °C (0.03

torr), mp 78 °C (lit.⁴⁰ 78–78.5 °C); **3b** ($R^1 = 1$ -cyclohexenyl, $R^2 = H$) bp 135-149 °C (0.1 torr), mp 76-79 °C.

Although the alkenylboranes thus obtained are stable to air and can be handled by the usual method, they decompose slowly at room temperature during storage for long periods. (Z)-1-Hexenylborane (14) was prepared from 1-bromohexyne and disiamylborane by the method of Campbell and Molander¹² and stored as a benzene solution.

Organic Halides. (E)- β -Bromostyrene from the Aldrich Chemical Co. was used without further purification. (Z)- β -Bromostyrene was prepared by the method of Cristol⁴¹ and was stored in a refrigerator. (E)- and (Z)-1-Octenyl bromides were prepared from 1-octyne by the methods of Miller⁴² and Brown.⁴³ Their isomeric purities were over 99%. α -Bro-mostyrene,⁴⁴ 2-methyl-1-propenyl bromide,⁴⁵ 1-bromohexyne,⁴⁶ 1bromooctyne,46 bromophenylethyne,47 and cinnamyl phenoxide48 were prepared by the reported procedures. Allyl chloride, cinnamyl chloride, and allyl phenoxide were used after distillation.

Palladium Complexes. The palladium(II) acetate used was a commercial product. Dichlorobis(triphenylphosphine)palladium(II) and tetrakis(triphenylphosphine)palladium(0) were prepared according to the reported procedures by Kharasch⁴⁹ and by Coulson.⁵⁰ The latter was stored in a sealed ampule under an argon atmosphere. Di-µ-chlorodiallyldipalladium(II), di-µ-acetatodiallyldipalladium(II),⁵¹ and (acetylacetonato)allylpalladium(II)⁵¹ were prepared by the method of Robinson and Shaw. trans-Chloro(trichloroethyl)bis(triphenylphosphine)palladi-

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 $um(II)^{52}$ was obtained from tetrachloroethylene and Pd(PPh₃)₄. trans-Methoxo(trichloroethenyl)bis(triphenylphosphine)palladium(II)²¹ was prepared by the Otsuka's method and used immediately after its preparation.

Reaction Conditions (Tables I and IV). The best conditions for the formation of conjugated alkadienes or alkenynes were determined by employing the following general procedure. The appropriate palladium complexes (0.01 or \sim 0.03 mmol) were placed in a flask containing a septum inlet, a reflux condenser, and an oil bubbler. The flask was flushed with nitrogen and filled with 3 mL of an appropriate solvent. One millimole of (E)- β -styryl bromide or 1-bromooctyne was then added by means of a hypodermic syringe through the septum inlet and stirred for 30 min at room temperature. Addition of 1-hexenyl-1,3,2-benzodioxaborole (1.1 mmol) or 1-hexenyldisiamylborane in THF (1.1 or 1.5 mmol) and an appropriate base were followed, and the resultant mixture was heated under reflux. After the reaction is over, the mixture was cooled to room temperature and the residual borane was oxidized with an aqueous solution (3 M, 0.3 mL) of NaOH-H₂O₂ (30% solution, 0.3 mL) for 1 h. The products were extracted with hexane, dried over MgSO₄, and analyzed directly by GLC. The products were determined by comparison with authentic samples. The results are shown in Tables I and İV

General Procedure for the Synthesis of (E,E)-Dienes (Table II). The following procedure for the preparation of (1E,3E)-3-ethyl-1-phenyl-1,3-hexadiene is representative.

In a dry 50-mL flask equipped with a magnetic stirring bar, a septum inlet, an oil bubbler, and a reflux condenser was placed Pd(PPh₃)₄ (0.058 g, 0.05 mmol). The flask was flushed with nitrogen and charged with 15 mL of dry benzene and β -styryl bromide (0.915 g, 5 mmol). After the solution was stirred for 30 min at room temperature, (3Z)-3-hexenyl-1,3,2-benzodioxaborole (1.11 g, 5.5 mmol) and NaOEt in EtOH (5 mL of a 2 M solution) were added, and the reaction mixture was then heated under reflux for 2 h. A white solid (probably NaCl) precipitated gradually. After completion of the reaction, aqueous NaOH (5 mL of a 3 M solution) was added at room temperature to the reaction mixture and then the mixture was stirred for 2 h in order to hydrolyze the boronic ester. The product was extracted with a 1:1 benzene-hexane solution, and the extracts were dried over anhydrous MgSO4. Analysis of the organic phase by GLC using tridecane as an internal standard indicated that (1E,3E)-3-ethyl-1-phenyl-1,3-hexadiene (4.65 mmol, 93%) was formed. The solvent was removed, and the residue was distilled under reduced pressure to give the diene (0.75 g, 81%); bp 138-139 °C (15 torr). An analytically pure sample was obtained by preparative GLC; n^{20} 1.5751; IR (neat) 1625, 1595, 960 cm⁻¹; ¹H NMR (CCl₄) δ 1.03 (t, 3 H), 1.08 (t, 3 H), 2.0–2.5 (m, 4 H), 5.54 (t, 1 H, J = 7 Hz), 6.41 (d, 1 H, J = 16 Hz), 6.66 (d, 1 H, J = 16 Hz), 7.1–7.5 (m, 5 H); MS, m/e(M⁺) obsd for C₁₄H₁₈ 186.1434, calcd 186.1431.

The dienes prepared by employing the above procedure are as follows. (1*E*,3*E*)-1-Phenyl-1,3-octadiene: n^{20} _D 1.5782; IR (neat) 1645, 1595, 990 cm⁻¹; ¹H NMR (CCl₄) δ 0.92 (t, 3 H), 1.1–1.7 (m, 4 H), 1.95–2.4 (m, 2 H), 5.72 (dt, 1 H, J = 7 and 15.5 Hz), 6.14 (dd, 1 H, J = 9 and 15.5 Hz), 6.33 (d, 1 H, 15.5 Hz), 6.66 (dd, 1 H, J = 9 and 15.5 Hz), 7.05–7.45 (m, 5 H); MS, m/e (M⁺) obsd for C₁₄H₁₈ 186.1426, calcd 186.1409.

(3*E*)-2-Phenyl-1,3-octadiene: n^{20}_D 1.5352; IR (neat) 1645, 1595, 975, 890, 780, 705 cm⁻¹; ¹H NMR (CCl₄) δ 0.91 (t, 3 H), 1.2–1.5 (m, 4 H), 1.95–2.25 (m, 2 H), 5.02 (d, 1 H, *J* = 2 Hz), 5.13 (d, 1 H, *J* = 2 Hz), 5.59 (dt, 1 H, *J* = 7 and 16 Hz), 6.27 (d, 1 H, *J* = 16 Hz), 7.24 (s, 5 H); MS, *m/e* (M⁺) obsd for C₁₄H₁₈ 186.1375, calcd 186.1406.

H); MS, m/e (M⁺) obsd for $C_{14}H_{18}$ 186.1375, calcd 186.1406. (4E)-2-Methyl-2,4-nonadiene: $n^{20}p$ 1.4697; IR (neat) 1625, 995, 965 cm⁻¹; ¹H NMR (CCl₄) δ 0.91 (t, 3 H), 1.15–1.50 (m, 4 H), 1.72 (s, 6 H), 1.8–2.2 (m, 2 H), 5.42 (dt, 1 H, J = 7.6 and 15 Hz); 5.67 (d, 1 H, J = 10 Hz), 6.12 (dd, 1 H, J = 10 and 15 Hz); MS, m/e (M⁺) for $C_{10}H_{18}$ obsd 138.1424, calcd 138.1409.

(1*E*)-1-Phenyl-4-methyl-1,3-pentadiene: n^{20}_{D} 1.6045; IR (neat) 1680, 1645, 1594, 990, 980 cm⁻¹; ¹H NMR (CCl₄) δ 1.85 (s, 6 H), 5.94 (d, 1 H, J = 11 Hz), 6.33 (d, 1 H, J = 18 Hz), 6.89 (dd, 1 H, J = 11 and 16 Hz), 7.1–7.35 (m, 5 H); MS, m/e (M⁺) 158.1100, for C₁₂H₁₄ obsd calcd 158.1105.

(5*E*,7*E*)-5,7-Tetradecadiene: n^{20}_{D} 1.4648; IR (neat 3010, 985 cm⁻¹; ¹H NMR (CCl₄) δ 1.91 (t, 3 H), 1.15–1.55 (m, 12 H), 1.85–2.20 (m, 4 H), 5.25–6.10 (m, 4 H); MS, *m/e* (M⁺) obsd for C₁₄H₂₆ 194.2000, calcd 194.2032.

(1*E*,3*E*)-1,4-Diphenyl-1,3-butadiene: mp 153 °C (lit.⁵⁷ 153 °C); IR (CCl₄) 1595, 985, 860 cm⁻¹; ¹H NMR (CCl₄) δ 6.4–7.1 (m, 4 H), 7.15–7.45 (m, 10 H). The spectrum of ¹H NMR was in good agreement with a commercial sample from Aldrich Chemical Co. MS, *m/e* (M⁺)

obsd for C₁₆H₁₄ 206.1077, calcd 206.1093.

Standard Procedure for the Synthesis of (E,Z)- and (Z,Z)-Dienes (Table III). The following procedure for the preparation of (1Z,3Z)-1-phenyl-1,3-octadiene is representative.

To a dry 50-mL flask equipped similarly with the case of the synthesis of (E,E)-dienes was placed Pd(PPh₃)₄ (0.174 g, 0.15 mmol), dry benzene (10 mL), and (Z)-B-styryl bromide (0.915 g, 5 mmol) under a nitrogen atmosphere. After the solution was stirred for 30 min, (Z)-1-hexenyldisiamylborane (6.5 mL of a 1 M solution in benzene, 6.5 mmol) and NaOEt in EtOH (5 mL of 2 M solution) were added by means of a hypodermic syringe through the septum inlet. Then the resultant mixture was heated under reflux for 2 h. The reaction mixture was cooled to room temperature. To the solution were added aqueous NaOH (2 mL of a 3 M solution) and then H_2O_2 (2 mL of 30% aqueous solution), and solution was then stirred for 1 h. The dienes were extracted with a 1:1 benzene-hexane solution and dried over anhydrous MgSO4. Analysis of the organic phase by GLC using tetradecane as an internal standard indicated that (1Z,3Z)-1-phenyl-1,3-octadiene (1.8 mmol, 36%) together with the (1Z, 3E) isomer (1.7%), (1E, 3Z) isomer (1.3%), and (1E, 3E)isomer (1.2%) were formed. Analytically pure sample was obtained by preparative GLC after distillation; bp 100-101 °C (2 torr); n²⁰_D 1.558; IR (neat) 1680, 1625, 1595, 1490 cm⁻¹; ¹H NMR (CCl₄) δ 0.93 (t, 3 H), 1.25-1.55 (m, 4 H) 2.1-2.4 (m, 2 H), 5.35-5.70 (m, 1 H), 6.25-6.60 (m, 3 H), 7.27 (s, 5 H); MS, m/e (M⁺) obsd for C₁₄H₁₈ 186.1392, calcd 186.1407. The ¹H NMR spectrum and the retention time on GLC of an authentic sample of (1Z, 3Z)-diene, prepared by the hydroborationprotonlysis⁵³ of 1-phenyl-1,3-octadiyne were in good agreements with those obtained by the above procedure. All other dienes were identified by comparison with their authentic samples. The following dienes were prepared from (E)-1-alkenyl-1,3,2-benzodioxaboroles or (Z)-1-hexenyldisiamylborane by the above procedure.

(12,3E)-1-Phenyl-1,3-octadiene: n^{20}_{D} 1.5582; IR (neat) 1640, 1595, 1490, 985 cm⁻¹; ¹H NMR (CCl₄) 0.85 (t, 3 H), 1.2–1.50 (m, 4 H), 1.9–2.25 (m, 2 H), 5.82 (dt, 1 H, J = 7 and 15 Hz), 6.20 (d, 1 H, J =10 Hz), 6.59 (dd, 1 H, J = 8 and 15 Hz) 6.34 (dd, 1 H, J = 8 and 10 Hz), 7.15–7.40 (m, 5 H); MS, m/e (M⁺) obsd for C₁₄H₁₈ 186.1409, calcd 186.1409.

(1*E*,3*Z*)-1-Phenyl-1,3-octadiene: n^{20}_{D} 1.5691; IR (neat) 1675, 1620, 1590, 1485, 980, 940 cm⁻¹; ¹H NMR (CCl₄) δ 0.95 (t, 3 H), 1.25-1.60 (m, 4 H), 2.1-2.45 (m, 2 H), 5.48 (dt, 1 H, *J* = 7 and 10.5 Hz), 6.12 (dd, 1 H, *J* = 10 and 10.5 Hz), 6.46 (d, 1 H, *J* = 15.5 Hz), 7.01 (dd, 1 H, *J* = 10 and 15.5 Hz) 7.2-7.45 (m, 5 H); MS, *m/e* (M⁺) 186.1424, for C₁₄H₁₈ obsd calcd 186.1408.

(5E,7Z)-5,7-Tetradecadiene: n^{20}_D 1.4651; IR (neat) 980, 945 cm⁻¹; ¹H NMR (CCl₄) δ 0.92 (t, 6 H), 1.21–1.55 (m, 12 H), 1.90–2.30 (m, 4 H), 5.05–6.45 (m, 4 H); MS, m/e (M⁺) 194.2024, for Cl₄H₂₆ obsd calcd 194.2032. The IR and ¹H NMR spectra were completely superimposable with those of the authentic sample prepared by the hydroboration-protonolysis^{53,54} of (5E)-tetradec-5-en-7-yne which was obtained by the cross-coupling described later.

(5Z,7Z)-5,7-Tetradecadiene: n^{20}_D 1.4657; IR (neat) 3045, 3010 cm⁻¹; ¹H NMR (CCl₄) δ 0.91 (t, 6 H), 1.15–1.50 (m, 12 H), 1.9–2.3 (m, 4 H), 5.39 (dt, 2 H, J = 7 and 10 Hz), 6.21 (d, 2 H, J = 10 Hz); MS, m/e(M⁺) 194.2027, for C₁₄H₂₆ obsd calcd 194.2032. The structure was identified by the direct comparison with the authentic sample synthesized by the literature procedure.⁵³

(1*E*,3*Z*)-1,4-Diphenyl-1,3-butadiene: mp 20–25 °C; IR (neat) 1675, 1620, 1590, 1490 cm⁻¹; ¹H NMR (CCl₄) δ 6.37 (d, 2 H, *J* = 8 Hz), 6.61 (d, 2 H, *J* = 15 Hz), 7.15–7.45 (m, 10 H), MS, *m/e* (M⁺) 206.1090, obsd for C₁₆H₁₄ 206.1093.

(12,3*E*)-1-Phenyl-4-(1-cyclohexenyl)-1,3-butadiene: IR (neat) 1615, 1595, 1490, 985, 940, 915 cm⁻¹; ¹H NMR (CCl₄) δ 1.5–1.8 (m, 4 H), 2.0–2.3 (m, 4 H), 5.81 (br s, 1 H), 6.24 (d, 1 H, *J* = 12 Hz), 6.34 (dd, 1 H, *J* = 8 and 12 Hz), 6.48 (d, 1 H, *J* = 15 Hz), 6.73 (dd, 1 H, *J* = 8 and 15 Hz). MS, *m/e* (M⁺) obsd for C₁₈H₁₈ 210.1380, calcd 210.1406.

(3Z)-2-Phenyl-1,3-octadiene: n^{20}_D 1.5381; IR (neat) 1640, 1600, 1495 cm⁻¹; ¹H NMR (CCl₄) 0.86 (t, 3 H), 1.2–1.6 (m, 4 H), 2.0–2.25 (m, 2 H), 5.11 (s, 1 H), 5.49 (s, 1 H), 5.67 (dt, 1 H, J = 7 and 11 Hz), 6.14 (d, 1 H, J = 11 Hz), 7.1–7.5 (m, 5 H); MS, m/e (M⁺) 186.1383, for C₁₄H₁₈ obsd calcd 186.1406.

General Procedure for the Synthesis of Enynes (Table V). The following procedure for the preparation of (5Z)-tetradec-5-en-7-yne is typical.

A 50-mL flask equipped similarly in the case of the synthesis of dienes was charged with $Pd(Ph_3)_4$ (0.174 g, 0.15 mmol), dry benzene (12 mL),

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and 1-bromooctyne (0.945 g, 5 mmol) under a nitrogen atmosphere. The reaction mixture was stirred for 30 min at room temperature, and to the solution were added (Z)-1-hexenyldisiamylborane (8 mL of a 0.75 M solution in benzene, 6 mmol) and NaOMe in MeOH (7 mL of a 1 M solution). The reaction mixture was heated under reflux for 2 h and then treated with aqueous NaOH (1.8 mL of a 3 M solution) and H_2O_2 (1.8 mL of a 30% solution) for 1.5 h at room temperature to remove the unreacted alkenylborane. The product was extracted with hexane and dried over MgSO₄. Analysis of the extracts by means of GLC indicated that 2.65 mmol (53%) of (5Z)-tetradec-5-en-7-yne was formed together with 0.13 mmol (2.6%) of (5E)-enyne. After the removal of the solvent the enyne purified by distillation; bp 86-87 °C (1 torr). An analytically pure sample was obtained by preparative GLC: n²⁰_D 1.4620; IR (neat) 3020, 2200, 1610 cm⁻¹; ¹H NMR (CCl₄) δ 0.93 (t, 3 H), 1.15–1.65 (m, 12 H), 2.05–2.45 (m, 4 H), 5.40 (d, 1 H, J = 11 Hz), 5.80 (dt, 1 H, J= 7 and 11 Hz); MS, m/e (M⁺) 192.1880, for C₁₄H₂₄ obsd calcd 192.1878.

The enynes, prepared by the above procedure using 1 mol % of catalyst and 10% excess of 1-alkenyldisiamylborane, are as follows.

(5*E*)-Tetradec-5-en-7-yne: n^{20}_{D} 1.4641; IR (neat) 3020, 2220, 955 cm⁻¹; ¹H NMR (CCl₄) δ 0.91 (t, 6 H), 1.11–1.70 (m, 12 H), 1.92–2.34 (m, 4 H), 5.33 (d, 1 H, J = 16 Hz), 5.94 (dt, 1 H, J = 6.5 and 16 Hz).Anal. Calcd for C14H24: C, 87.42; H, 12.58. Found: C, 87.27; H, 12.59.

(3E)-1-Phenyloct-3-en-1-yne: n^{20}_{D} 1.5619; IR (neat) 3020, 2200, 955 cm^{-1} ; ¹H NMR (CCl₄) δ 0.93 (t, 3 H), 1.20–2.05 (m, 4 H), 2.15 (q, 2 H), 5.62 (d, 1 H, J = 16 Hz), 6.17 (dt, 1 H, J = 6.5 and 16 Hz), 7.24 (m, 5 H). Anal. Calcd for C₁₃H₁₆: C, 90.64; H, 9.36. Found: C, 90.47; H, 9.33

(3E)-1-Phenylpent-3-en-1-yne: n²³_D 1.5948; IR (neat) 3020, 2215, 955 cm⁻¹; ¹H NMR (CCl₄) δ 1.82 (d, 3 H, J = 6.5 Hz), 5.55 (d, 1 H, J = 16 Hz), 6.09 (dq, 1 H, J = 6.5 and 16 Hz), 7.21 (m, 5 H); MS, m/e142 (M⁺), 117, 103, 89. Anal. Calcd for $C_{11}H_{10}$: C, 92.91; H, 7.09. Found: C, 92.80; H, 7.05.

(1E)-1-Phenyldec-1-en-3-yne: n²⁰ 1.5643; IR (neat) 3025, 2215, 955 cm^{-1} ; ¹H NMR (CCl₄) δ 0.92 (t, 3 H), 1.16–1.79 (m, 8 H), 2.33 (m, 2 H), 6.06 (dt, 1 H, J = 2 and 16 Hz), 6.90 (d, 1 H, J = 16 Hz), 7.28 (m, 5 H); MS, m/e 212 (M⁺), 183, 169, 155, 141, 128, 115, 91. Anal. Calcd for C₁₆H₂₀: C, 90.50; H, 9.50. Found: C, 90.38; H, 9.47.

Reaction of 1-Hexenyl-1,3,2-benzodioxaborole with Allylic Compounds (Table VI). In a 25-mL flask was placed a mixture of Pd(PPh₃)₄ (0.058 g, 0.05 mmol), (E)-1-hexenyl-1,3,2-benzodioxaborole (0.222 g, 1.1 mmol), and allylic compounds (1 mmol) in 5 mL of dry benzene in an atmosphere of nitrogen. After the reaction mixture was heated under reflux for 2 h, the reaction mixture was analyzed directly by GLC on a

SE-30 column by comparison with the authentic sample.²⁷ The results are shown in Table VI.

Reaction of 1-Octenylboranes with Palladium Complexes (Table VII). In a 25-mL flask was placed palladium complexes (1.0 mmol) and dry THF under a nitrogen atmosphere. To this solution was added (E)-1octenyl-1,3,2-benzodioxaborole (0.253 g, 1.1 mmol) or (E)-1-octenyldisiamylborane (1.1 mL of a solution in THF, 1.1 mmol) dropwise, and the solution was stirred at room temperature. To the solution was then added an appropriate amount of decane in the reaction using the π -allylpalladium complex or tridecane in the reaction using (trichlorovinyl)palladium complex, and the reaction mixture was analyzed directly by GLC on SE-30 column. The products were determined by comparison with authentic samples. Preparation of 1,4-undecadiene had been described elsewhere.55 1,1,2,2-Trichloro-1,3-decadiene was prepared by the following procedure.

In a 50-mL flask was placed Pd(PPh₃)₄ (0.104 g, 0.09 mmol) in benzene (10 mL), tetrachloroethylene (0.51 mL, 5 mmol), (E)-1-octenyl-1,3,2-benzodioxaborole (0.758 g, 3.3 mmol), and NaOEt in EtOH (3 mL of a 2 M solution), and the reaction mixture was heated under reflux for 4 h. To the solution was then added aqueous NaOH (4 mL of a 3 M solution), and the mixture was stirred for 2 h at room temperature. After the usual workup, the diene was extracted with hexane and dried over MgSO₄. Distillation of the products gave 0.247 g (31%) of the corresponding diene: bp 142 °C (15 torr). An analytically pure specimen was obtained by preparative GLC: IR (neat) 1725, 1635, 1550, 955, 125 cm⁻¹; ¹H NMR (CCl₄) δ 0.89 (t, 3 H), 1.10–1.50 (m, 8 H), 1.0-2.4 (m, 2 H), 6.27 (dt, 1 H, J = 7 and 15 Hz), 6.59 (d, 1 H, J =15 Hz); MS, m/e (M⁺) obsd for C₁₀H₁₅Cl₃ 240.0289, 242.0242, 244.0132, 246.0164, calcd 240.0239, 242.0210, 244.0178, 246.0151.

Reaction of Lithium 1-Hexenylmethyldisiamylborate with (E)- β -Styryl Bromide (Equation 13). A dried 25-mL flask was charged with Pd-(PPh₃)₄ (0.0578 g, 0.05 mmol), dry THF (2 mL), and (E)-β-styryl bromide (0.183 g, 1 mmol). To this mixture was added lithium 1-hex-enylmethyldisiamylborate⁵⁶ in THF (3 mL of a 0.45 M solution), and the mixture was then refluxed for 3 h. The remaining borane was then oxidized with aqueous NaOH (0.5 mL of a 3 M solution) and 30% H₂O₂ (0.5 mL) for 1 h at room temperature. Analysis of the organic phase by GLC showed the formation of 1-phenyl-1,3-octadiene (9%) together with small amounts of 1-phenyl-1-propene and 2,3-dimethyl-4-nonene.

Trifluoroethylidynesulfur Trifluoride, CF₃C=SF₃, and Its Dimer

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Abstract: CF₃C=SF₃, the first species with a sulfur-carbon triple bond, has been prepared by dehydrofluorination of CF₃CH=SF₄ or CF₃CH₂SF₅. It is a colorless gas with mp -122.8 °C and an estimated bp -15 °C. Its molecular structure has been determined by a single-crystal X-ray investigation at -130 °C (space group $P2_1$; a = 6.298 Å, b = 7.599 Å, c = 5.667 Å, $\beta = 105.59^\circ$, Z = 2,608 observed reflections, R = 0.05). The molecule exhibits a very short C=S bond (1.394 Å) and an almost linear C-C=S geometry (171.5°). The triple bond reacts with HF to form the starting materials. On warming up slowly to -30 °C dimerization is observed. The dimer has been analyzed by X-ray crystallography at -122 °C (space group $P2_1/n$; a =12.808 Å, b = 5.612 Å, c = 6.571 Å, $\beta = 90.13^{\circ}$, Z = 2, 952 observed reflections, R = 0.045). The molecule is a butene $CF_3(SF_3)C = C(CF_3)SF_3$ with trans (E) configuration. This molecule is probably formed when $CF_3C = SF_3$ is internally cleaved into a carbene $CF_3 - \overline{C} - \overline{S}F_3$. NMR data and other physical measurements of these novel materials are given.

Introduction

 $CH_2 = SF_4^1$ and its derivatives $CH_3C = SF_4^2 CF_3 CH = SF_4^3$ and $CF_3(CH_3)C = SF_4^3$ have strong, almost nonpolar carbonsulfur double bonds within a very distinct geometry.^{4,5} Some of these alkylidene sulfur tetrafluorides turned out to be remarkably stable materials. Soon after the discovery of CH₂=SF₄ the question arose if triple-bonded systems would be capable of existence. Early attempts to generate HC=SF₃ by HF cleavage

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