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Stereodefined Construction of Trisubstituted Alkenes by Direct Coupling Reaction of Allylating Agents, Alkynes, and Organoboranes

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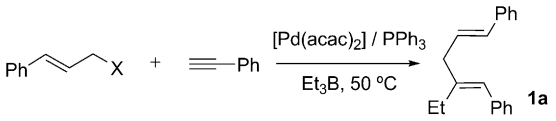
Stereodefined construction of C–C multiple bonds through carbometallation is among the most challenging and significant synthetic strategies in organic and organometallic chemistry.[1] In particular, alkenylboranes are valuable and salient active species for the Suzuki–Miyaura cross-coupling reaction, which affords tri- and tetrasubstituted alkenes as efficient functional materials.[2] Therefore, highly regio- and stereocontrolled preparations of alkenylboranes by means of hydroboration of alkynes and migration of alkynylborates have been developed.[3]

Previously, we have demonstrated the direct allylic activation of allyl alcohols, promoted by a combination of a Pd catalyst and Et_3B, to form a π-allylpalladium intermediate.[4] This species serves as an allyl cation equivalent for a wide variety of soft nucleophiles, facilitating electrophilic allylation (Tsuji–Trost reaction). In the absence of nucleophiles, the π-allylpalladium species undergoes an allyl–ethyl exchange reaction; this provides allyl diethylborane as an allyl-anion equivalent, which in turn reacts with aldehydes, acetals, and aldimines to give homoallyl alcohols and homoallylamines (Umpolung of π allylpalladium).[5] Thus, the combination of a Pd^0 catalyst and Et_3B works for the generation of both allyl cation and allyl anion equivalents directly from allylic alcohols to achieve amphiphilic allylic alkylations.[6]

Herein, we report a similar reaction system by using trialkylboranes and allylic alcohols with terminal alkynes in the presence of a Pd^0 catalyst, which evoked a three-component coupling reaction of alkyne, allyl, and alkyl groups to give (*E*)-1-substituted 2-alkyl-1,4-pentadienes involving geminal alkylation and allylation at the acetylenic terminal carbon atom with high regio- and stereoselectivities. In this case, it is notable that trialkylboranes serve as not only alkylating components for the coupling reaction, but also promoters for the oxidative addition of allylic alcohols toward Pd^0 catalyst forming π-allylpalladium intermediates. Moreover, we disclose herein, that bis-dienes can act as allylating agents to undergo the multicomponent coupling reactions accompanying dimerization of diene moieties to give cyclic alkanes and heterocyclic compounds possessing dienyl and alkenyl side chains in excellent regio- and stereoselectivities.

The scope and limitation for the initial reactions were determined in the presence of a catalytic amount of $[Pd(acac)_2]$ and PPh_3 at 50 °C under nitrogen atmosphere. The results of the coupling reaction of phenylacetylene with phenyl-substituted allylating agents and Et_3B are summarized in Table 1.[7]

Table 1. Pd-catalyzed three-component coupling of phenylacetylene, allylating agents, and triethylborane.[a]



Entry	Allylating agent X	*t* [h]	Yield **1a** [%]
1	Cl	72	0
2	OAc	30	0[b]
3	OCO_2Me	50	62 [single]
4	OH	30	81 [single]

[a] The reaction was performed in the presence of phenylacetylene (1 mmol), allylating agent (2 mmol), $[Pd(acac)_2]$ (0.025 mmol), PPh_3 (0.05 mmol), and Et_3B (2.4 mmol) in THF (0.5 mL) at 50 °C. [b] (1*E*,4*Z*)-1,4-Diphenylhepta-1,4-diene (**1a′**) was obtained as a regioisomer in 41% yield.

The reaction outcome depends on the type of leaving group of the allylating agents. The stronger the basicity of the leaving group, the higher the yield of the expected product. Cinnamyl chloride inhibited the expected reaction, and phenylacetylene was recovered quantitatively (Table 1, entry 1). Cinnamyl acetate showed the electrophilic allylation at the β-carbon of alkynylborate to give 1,4-diphenylhepta-1,4-diene **1a′**, which has been previously reported by Murakami group (Table 1, entry 2).[3i] Methyl carbonate gave the desired three-component coupling product, 1-phenyl-2-ethyl-1,4-pentadiene (**1a**) as a single isomer in reasonable yield (Table 1, entry 3). The similar coupling reaction proceeded smoothly by employment of cinnamyl alcohol as an allylating agent to give **1a** in good yield with excellent regio- and stereoselectivities (Table 1, entry 4).

Allylation of phenylacetylene with a wide structural variety of substituted allylic alcohols and tributylborane was studied under similar conditions (Table 2). Crotyl alcohol and

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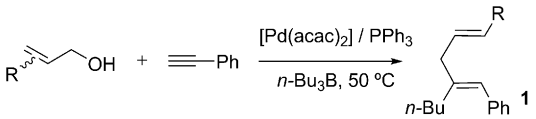
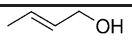
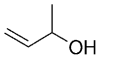
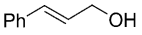
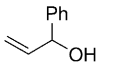
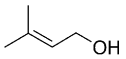
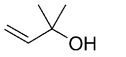
Table 2. Pd-catalyzed three-component coupling of phenylacetylene, allylic alcohols, and tributylborane.[a]



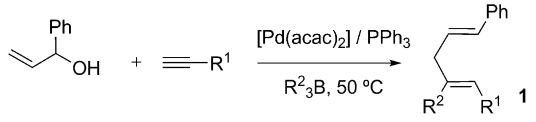
Entry	Allyl alcohol	Yield **1** [%]
1		**1b-*l***[b]: 77, **1b-*b***[b]: 9
2		**1b-*l***[b]: 80, **1b-*b***[b]: 11
3		**1c**: 67
4		**1c**: 78
5		**1d**: 32
6		**1d**: 53

[a] The reaction was performed in the presence of phenylacetylene (1 mmol), allylic alcohol (2 mmol), $[Pd(acac)_2]$ (0.025 mmol), PPh_3 (0.05 mmol), and nBu_3B (2.4 mmol) in THF (0.5 mL) at 50 °C for 48 h. [b] **1b-*l*** and **1b-*b*** represent the linear and branched regioisomers, respectively.

α-methallyl alcohol provided the linear allylated product as major isomer along with the branched allylation isomer with similar regio- and stereoselectivities (Table 2, entries 1 and 2). Both cinnamyl alcohol and α-phenylallyl alcohol underwent the expected coupling reaction at less substituted allylic position to afford **1c** in good yields as a single product (Table 2, entries 3 and 4). Prenyl alcohol and α,α-dimethyl allyl alcohol also provided the less substituted allylation product **1d** as a single isomer in reasonable yields (Table 2, entries 5 and 6).

Furthermore, we investigated the Pd-catalyzed three-component coupling reaction of α-phenylallyl alcohol with various alkynes and organoboranes (Table 3). It was found that the terminal alkynes are indispensable to the coupling reaction, whereas no reaction took place with internal alkynes, for example, 3-hexyne (not shown in Table 3). The abstraction of the acetylenic terminal hydrogen atom to form an alkynylborate species might be required to promote the coupling reaction. Aliphatic substituted alkynes provided the desired products as a mixture of *E* and *Z* isomers in 4:1 to 6:1 ratios (Table 3, entries 1–4). An unprotected alkynyl alcohol participated in the reaction to give **1h** without undergoing electrophilic allylation on the hydroxy group (Table 3, entry 4).

Table 3. Pd-catalyzed three-component coupling of various alkynes, allyl alcohol, and trialkylboranes.[a]

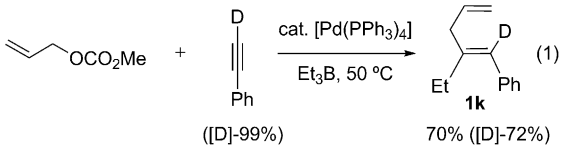


Entry	Alkyne R^1	Borane R^2	*t* [h]	Yield [%] (*E*/*Z*)
1	$(CH_2)_3CN$	Et	72	**1e**: 82 (4:1)
2	nC_7H_{15}	Et	28	**1f**: 66 (6:1)
3	$(CH_2)_2OBz$	Et	15	**1g**: 78 (4:1)
4	$(CH_2)_2OH$	Et	24	**1h**: 64 (4:1)
5	Ph	nC_6H_{13}[b]	24	**1i**: 58 (single)
6	Ph	nC_6H_{13}[c]	24	**1i**: 75 (single)
7	Ph	$PhCH_2CH_2$[d]	24	**1j**: 76 (single)

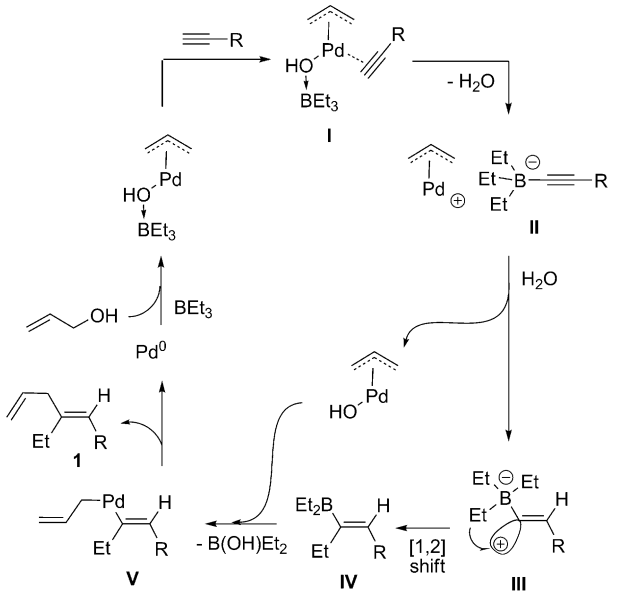
[a] The reaction was performed in the presence of alkyne (1 mmol), allylic alcohol (2 mmol), $[Pd(acac)_2]$ (0.025 mmol), PPh_3 (0.05 mmol), and organoborane (2.4 mmol) in THF (0.5 mL) at 50 °C. [b] $(nC_6H_{13})_3B$ was prepared by hydroboration of 1-hexene and diborane. [c] *B*-$(PhCH_2CH_2)$-9-BBN was prepared by hydroboration of 1-hexene with 9-BBN. [d] *B*-$(PhCH_2CH_2)$-9-BBN was prepared by hydroboration of styrene with 9-BBN.

The reactions with various alkylboranes were examined. Tri(*n*-hexyl)borane gave the corresponding allylic product **1i** in moderate yield (Table 3, entry 5), whereas *B*-(*n*-hexyl)-9-BBN (BBN = borabicyclo[3.3.1]nonane) prepared by hydroboration of 1-hexene with 9-BBN was more effective to give rise to **1i** in reasonable yield (Table 3, entry 6). *B*-Phenethyl-9-BBN could serve as an alkylating agent, and the phenethyl group migrated to the acetylenic terminal carbon atom from the boron atom with excellent regio- and stereoselectivities (Table 3, entry 7). Thus, the numerous organoboranes were applicable to the three-component coupling reactions with a wide variety of allylic alcohols and terminal alkynes.

To gain insight into the reaction mechanism, a deuterium-labeling experiment was performed. 1-Deuterio phenyl acetylene ([D]-99%) underwent the coupling reaction by treatment with allyl methyl carbonate and Et_3B in the presence of Pd^0 catalyst in dry THF under nitrogen atmosphere [Eq. (1)]. The allylated product, 1-phenyl-2-ethyl-1,4-pentadiene (**1k**), incorporated deuterium at the vinylic position, affording ([D]-72%) in reasonable yield. Although the reason for incomplete incorporation of deuterium is not clear at present, this result suggests that the proton source at the vinylic position might owe its origin to the acetylenic terminal proton giving rise to trisubstituted alkenes with high regio- and stereoselectivities.



Even though it is premature to speculate on the reaction mechanism based on the deuterium-labeling experiment, a plausible reaction mechanism for the three-component coupling process with allyl alcohol, phenylacetylene, and Et_3B might be illustrated in Scheme 1. Et_3B promotes the oxidative addition of an allyl alcohol upon treatment with Pd^0 catalyst to form the π-allylpalladium intermediate, which coordinates to the alkyne as a Lewis acid to form π-alkyne palladium complex **I**, thus increasing the acidity of the acetylenic terminal proton. The abstraction of the proton from the activated terminal alkyne is induced by the OH group acting as a base to give rise to the π-allylpalladium alkynylborate intermediate **II**. The alkynyltriethylborate **II** undergoes protonation at the β-carbon position to give

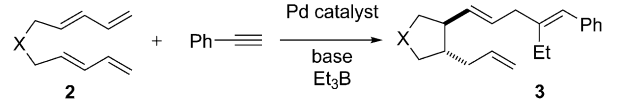


Scheme 1. Plausible reaction mechanism for three-component coupling reaction of alkyne, Et_3B, and allyl alcohol.

a vinylic cation intermediate **III**, which then experiences [1,2] ethyl group migration to the empty p orbital of the vinylic carbocation with excellent stereoselectivity to form vinyldiethylborane intermediate **IV**.[8] Transmetallation of the vinyldiethylborane **IV** with the π-allylpalladium species affords an allylvinylpalladium intermediate **V** followed by reductive elimination to give 1,4-pentadiene (**1**) with extremely high regio- and stereoselectivities accompanying the regeneration of the Pd^0 catalyst as an active species.

A series of these reaction systems were applied to the coupling reaction of bis-dienes tethered by tosylamide, oxygen atom, and malonate functional groups for tandem cyclizations. The results of the coupling reaction of bis-diene **2**, phenylacetylene, and Et_3B in THF at room temperature are presented in Table 4.

Table 4. Pd-catalyzed three-component coupling of various bis-dienes **2**, phenylacetylene, and triethylborane.[a]



2 **3**

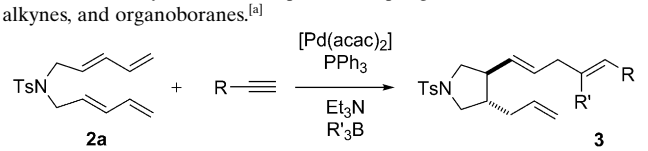
Entry	Diene **2**	Pd catalyst	Base	Yield **3** [%]
1	NTs	$[Pd(PPh_3)_4]$	none	**3a**: 0
2	NTs	$[Pd(PPh_3)_4]$	Et_3N	**3a**: 66
3	NTs	$[Pd(acac)_2]$	none	**3a**: 0
4	NTs	$[Pd(acac)_2]$	Et_3N	**3a**: 84
5	NTs	$[Pd(acac)_2]$	*t*BuOK	**3a**: 0
6	NTs	$[Pd(acac)_2]$	K_2CO_3	**3a**: 37
7	$C(CO_2Me)_2$	$[Pd(acac)_2]$	Et_3N	**3b**: 88
8	$C(CO_2Et)_2$	$[Pd(acac)_2]$	Et_3N	**3c**: 99
9	O	$[Pd(acac)_2]$	Et_3N	**3d**: 73

[a] The reaction was performed in the presence of phenylacetylene (1 mmol), bis-diene **2** (0.5 mmol), Pd catalyst (0.025 mmol), PPh_3 (0.05 mmol in entries 3–9; 0 mmol in entries 1 and 2), Et_3B (2.4 mmol), and base (3 mmol) in THF (0.5 mL) at RT.

The reaction was undertaken with various kinds of Pd complexes and bases. In the absence of base, the desired reaction did not proceed at all and the bis-diene was recovered almost quantitatively (Table 4, entries 1 and 3). Triethylamine accelerated the multicomponent coupling reaction involving the tandem cyclization of diene moiety giving rise to *trans*-3-allyl-4-pentadienyl pyrrolidine (**3a**) as a single isomer (Table 4, entries 2 and 4). Among these reactions with organic and inorganic bases, it was clarified the combination of $[Pd(acac)_2]$ and PPh_3 with triethylamine is the best condition for the multicomponent coupling reaction with bis-dienes (Table 4, entries 1–6). Bis-dienes **2** tethered by dimethylmalonate, diethylmalonate, and oxygen atom could participate in the similar reactions to give cyclized products **3b–d**, consisting of cyclopentane and THF frameworks with high regio- and stereoselectivities (Table 4, entries 7–9).

Table 5 summarizes the results of a wide structural variety of alkynes and organoboranes with bis-diene **2a** under the optimized conditions of Table 4. In spite of aromatic and aliphatic alkynes, the stereodefined pyrrolidines **3e** and **3f** were constructed as a single isomer (Table 5, entries 1 and 2). It is significant that the terminal alkynes with hydroxy group and oxygen atom at their substituents tolerate the coupling reaction with excellent regio- and stereoselectivities in contrast to the result of Table 3. Organoboranes prepared by hydroboration of 1-alkenes with diborane could take part in the coupling reaction in good-to-quantitative yields (Table 5, entries 5–8).

Table 5. Pd-catalyzed three-component coupling of bis-diene **2a**, various alkynes, and organoboranes.[a]

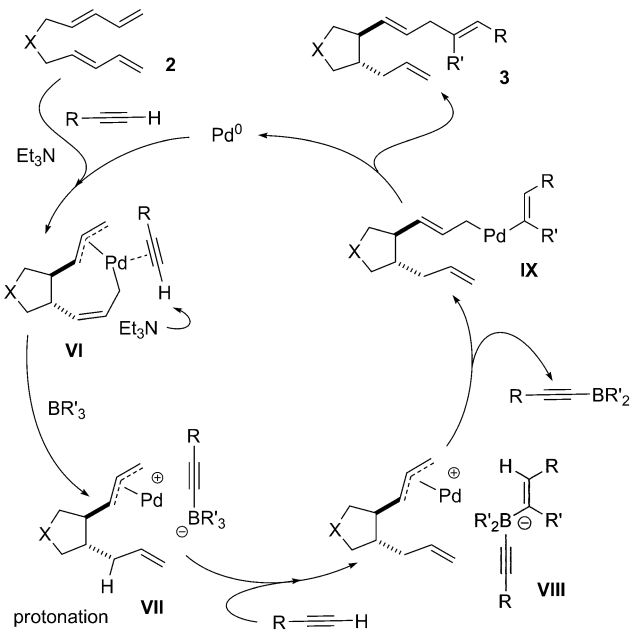


2a **3**

Entry	Alkyne R	Alkylborane R′	Yield **3** [%]
1	*p*-Anis	Et	**3e**: 80
2	nC_7H_{15}	Et	**3f**: 52
3	$(CH_2)_2OBn$	Et	**3g**: 65
4	$(CH_2)_2OH$	Et	**3h**: 70
5	Ph	*n*Bu	**3i**: 78
6	Ph	*n*Hex[b]	**3j**: 99
7	Ph	$Ph(CH_2)_2$[b]	**3k**: 100
8	Ph	$Ph(CH_2)_3$[b]	**3l**: 88

[a] The reaction was performed in the presence of alkyne (1 mmol), bis-diene **2a** (0.5 mmol), $[Pd(acac)_2]$ (0.025 mmol), PPh_3 (0.05 mmol), organoborane (2.4 mmol), and Et_3N (3 mmol) in THF (0.5 mL) at RT. [b] Trialkylboranes were prepared by hydroboration of their corresponding 1-alkenes with diborane.

A plausible reaction mechanism for the multicomponent coupling reaction with alkyne, trialkylborane, and bis-diene is illustrated in Scheme 2. Pd^0 catalyzes dimerization of bis-diene constituents involving *anti* cyclization to give η^1,η^3-bis-allylpalladium intermediate **VI**,[9] which then serves as allyl cation equivalent followed by highly regio- and stereocontrolled coupling reaction with alkynylborate in similar



Scheme 2. A plausible reaction mechanism for multicomponent coupling reaction of alkyne, trialkylborane, and bis-diene **2**.

manner to the reaction mechanism shown in Scheme 1. Base is required for the generation of alkynylborates through abstraction of more acidic hydrogen atom of terminal alkyne coordinated to η^1,η^3-bis-allylpalladium(II) complex at the initial reaction stage. Pd^0 active species would be liberated by reductive elimination of allylvinylpalladium intermediate **IX** giving cyclized product **3** as a single isomer.

In summary, we have developed the Pd-catalyzed three-component coupling reaction of allylic alcohols, organoboranes, and terminal alkynes giving 1-substituted 2-alkyl-1,4-pentadienes with complete control of regio- and stereoselectivities. Under similar conditions, bis-diene undergoes the tandem multicomponent coupling reaction accompanying intramolecular dimerization of bis-π-allylpalladium moiety to give rise to *trans*-allyl pentadienyl cyclic compounds with excellent regio- and stereoselectivities. The application and extension of these methods for the synthesis of physiologically active molecules and natural products, such as prostanoids, will be reported in due course.

Experimental Section

General procedure (Table 1, entry 4): A two-necked round-bottomed flask (25 mL) equipped with a rubber septum and an air condenser, at the top of which was attached a three-way stopcock fitted a nitrogen balloon, was charged with [Pd(acac)$_2$] (7.6 mg, 0.025 mmol) and PPh_3 (13.1 mg, 0.05 mmol). The apparatus was purged with nitrogen, and the flask was charged with freshly distilled THF (0.5 mL). To this solution, phenylacetylene (102 mg, 1 mmol), cinnamyl alcohol (268 mg, 2 mmol), and Et_3B (2.4 mL of 1 M hexane solution; 2.4 mmol) were successively added while stirring the solution with a magnetic stirrer. The stirring was continued for 30 h at 50 °C. After the reaction was completed, the reaction mixture was diluted with ethyl acetate (20 mL). The organic phase was washed with saturated $NaHCO_3$ (2×20 mL) and brine (2×20 mL), then dried over magnesium sulfate, filtered, and concentrated. The residue was subjected to column chromatography over silica gel (Wako gel C-300, hexane as eluent) to give **1a** in 81% yield.

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Keywords: alkynes · allylation · boron · palladium · synthetic methods

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