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The Palladium-Catalyzed Cross-Coupling Reaction of Organosilicon Compounds with Allylic Carbonates or Diene Monoxides

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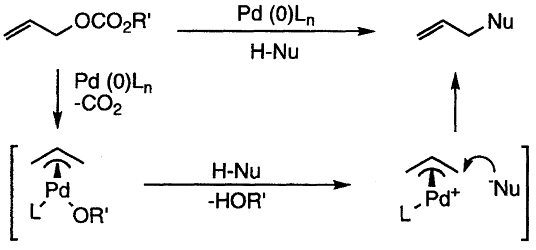
The cross-coupling reaction of allylic carbonates with organosilanes was found to proceed without fluoride ion activation under mild conditions by using a coordinatively unsaturated palladium complex as a catalyst. The reaction was assumed to proceed through an allylpalladium alkoxide derived from the allylic carbonate substrate and a palladium(0) species, the alkoxo ligand activating the organosilicon reagent. Likewise, diene monoxides also underwent cross-coupling with alkenyl- and arylfluorosilanes in moderate to high yields.

The cross-coupling reaction of an organometallic reagent with an organic electrophile is a straightforward method for synthesizing the carbon skeleton of various useful target molecules. To this transformation, various kinds of metal reagents are applicable.[1)]

We have been studying the palladium catalyzed cross-coupling reaction of organosilicon compounds using a fluoride ion activator.[2)] The success of the reaction heavily depends on the activation of a less polar carbon–silicon bond by a fluoride ion to generate a reactive pentacoordinate silicate species. Thus, the use of a stoichiometric amount of fluoride ion is essential. We studied the organosilicon-based cross-coupling reaction using various allylic electrophiles.

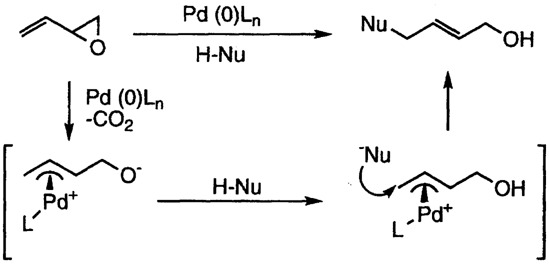
The carbon–carbon bond formation between a variety of allylic electrophiles and carbonaceous nucleophiles using a palladium catalyst has been extensively documented during the past two decades.[3)] The allylic substitution usually takes place by an attack of a nucleophile at the allylic carbon. As the substrate, allylic carbonates are unique with respect to the following features: (1) An η^3-allylpalladium alkoxide intermediate is involved whose alkoxide ligand can behave as a catalytic base; (2) Thus, the reaction proceeds under neutral conditions;[4)] (3) Various organometallic reagents can couple with allylic electrophiles. The catalytic reaction is illustrated in Scheme 1.



Scheme 1.

In a similar way, diene monoxides, upon treatment with a palladium catalyst, afford η^3-allylpalladium alkoxide intermediates, whose allyl and alkoxide moieties are connected directly. The intermediates then undergo coupling with carbonaceous nucleophiles to preferentially give 1,4-products.[5)] Scheme 2 illustrates the generally accepted reaction pathway.

We envisaged that the η^3-allylpalladium alkoxide intermediate shown in Scheme 1 might activate an organosilicon compound in a catalytic way.[6)] The hypothetical reaction pathway is schematically shown in Scheme 3. If the alkoxide ion of the η^3-allylpalladium alkoxide produced from an allylic carbonate and a Pd(0) catalyst can attack an organosilane R–SiY$_3$, an ion pair of a cationic η^3-allylpalladium and a pentacoordinated silicate would be produced. This intermediate, if transmetallation takes place smoothly, would give an η^3-allyl(organo)palladium (η^3-C$_3$H$_5$)PdRL. The final reductive elimination would afford a cross-coupled product with the Pd(0) species being regenerated.



Scheme 2.

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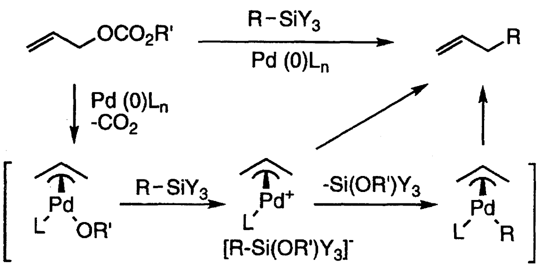
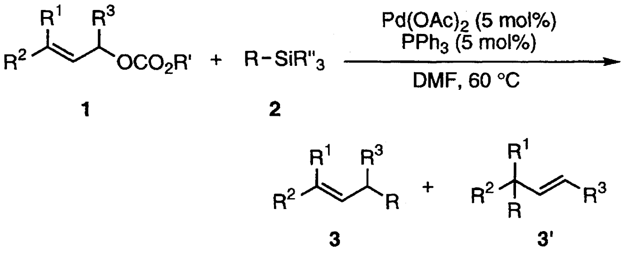


Scheme 3.

We also contemplated that a similar reaction might take place with a 1,3-diene monoxide, as shown in Scheme 4.

We describe herein the synthetic and mechanistic aspects of the palladium catalyzed cross-coupling reaction of allylic carbonates[6] or diene monoxides with organosilanes in the absence of a fluoride ion activator. Although the cross-coupling of allylic carbonates or diene monoxides has been studied with some organometallic reagents,[7] that using an organosilicon compound and involving a catalytic η^3-allylpalladium species has rarely been studied.[8]

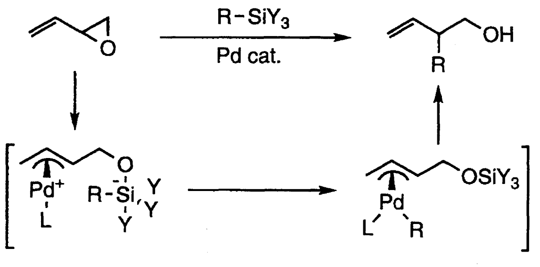


(1)

Results and Discussion

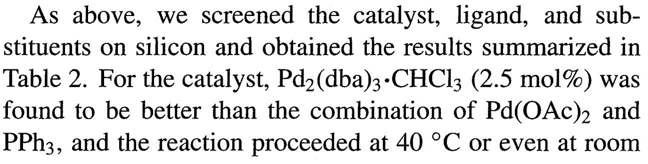
Coupling Reaction of Allylic Carbonates. We started by examining the reaction of cinnamyl ethyl carbonate (**1a**) with dimethyl(fluoro)[(*E*)-1-octenyl]silane (**2a**); screened the palladium catalyst, ligand, leaving group, and substituent(s) on silicon atom; and found that use of palladium(II) acetate and triphenylphosphine in *N*,*N*-dimethylformamide (DMF) at 60 °C was extremely effective. However, this reaction was proved to be sensitive to the ratio of the palladium to the phosphine ligand.

As summarized in Table 1, the reaction of **1a** with **2a**, performed in the presence of $Pd(OAc)_2$ (5 mol%) and PPh_3 (5 mol%) in DMF at 60 °C, afforded the expected cross-coupled product **3a** in 72% yield with retention of the olefin configuration (Run 1). When PPh_3 (10 mol%) was used for this reaction, the yield of **3a** decreased drastically, and cinnamyl ethyl ether was obtained along with unidentified by-products. The reaction using a $Pd(PPh_3)_4$ catalyst was sluggish to give **3a** in only 9% yield with unidentified materials in significant amounts (Run 2). The substituent on silicon affected the reaction remarkably. Whereas difluoro(methyl)[(E)-1-octenyl]silane (**2a′**) also exhibited a sufficient reactivity, trimethyl(vinyl)silane (**2a″**) was totally inert under the reaction conditions (Runs 3 and 4). This tendency is similar to the cross-coupling of alkenylsilanes assisted by a fluoride ion.[9] Fluoro(dimethyl)[(*E*)-2-phenylethenyl]silane (**2b**) and difluoro(methyl)[(*E*)-2-phenylethenyl]silane (**2b′**) gave similar results, and coupled product **3b** was isolated in high yields (Runs 5 and 6). The leaving group of allylic carbonates also affected the reaction. Although both ethyl carbonate **1a** and isopropyl carbonate **1a′** were favorable substrates (Runs 1 to 7), phenyl carbonate **1a″** did not undergo the expected cross-coupling reaction, but gave cinnamyl phenyl ether in a quantitative yield (Run 8).[10,11] The reaction of trisubstituted vinylsilane **2c** slowly proceeded at 90 °C to provide **3c** in 40% yield with the recovery (31%) of **1a** (Run 9). When ethyl 1-methyl-2-propenyl carbonate (**1b**) was allowed to react with **2b′** under the optimum conditions, a 4.4 : 1 regioisomeric mixture of products **3d** and **3d′** resulted (Run 10). Thus, the coupling at a less hindered site of an allylic system is preferred. The same regiochemical preference was observed with **1c**, **1d**, and **1e** (Runs 11—13). It is worth noting that allylic carbonate **1e** containing a siloxyl group also underwent a reaction without any cleavage of the silyl protecting group (Run 13), in sharp contrast to the fluoride ion-assisted reactions which often cause the removal of the silyl group in a competitive manner.



Scheme 4.

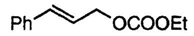
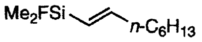
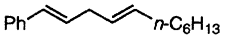
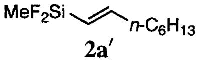
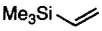
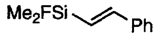
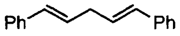
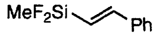
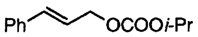
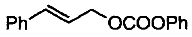
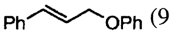
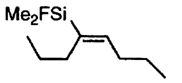
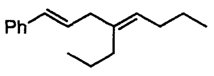
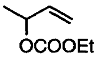
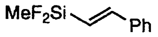
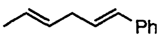
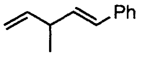
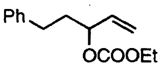
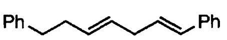
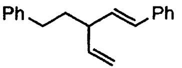
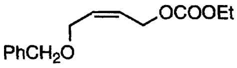
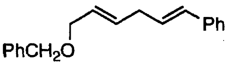
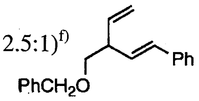
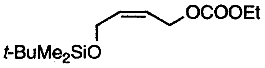
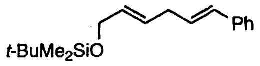
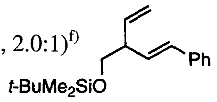
When aryl(ethyl)difluorosilane **4** was used in place of **2**, an allyl–aryl coupling reaction was readily achieved.



(2)

As above, we screened the catalyst, ligand, and substituents on silicon and obtained the results summarized in Table 2. For the catalyst, $Pd_2(dba)_3 \cdot CHCl_3$ (2.5 mol%) was found to be better than the combination of $Pd(OAc)_2$ and PPh_3, and the reaction proceeded at 40 °C or even at room temperature to provide **5a** in 84—91% yields (Runs 1—3). Although fluoro(dimethyl)phenylsilane (**4a′**) and trifluoro(phenyl)silane (**4a″**) also gave **5a**, a longer reaction time and higher temperatures were required (Runs 4 and 5). Thus, two fluorine atoms on silicon were concluded to be essential for smooth coupling. This substituent tendency parallels that of the fluoride ion-mediated coupling reaction of arylsilanes.[12] In addition to **4a**, ethyl(difluoro)(2-thienyl)silane (**4b**), ethyl(difluoro)(2,5-dimethoxyphenyl)silane (**4c**), and ethyl(di-

Table 1. Cross-Coupling Reaction of Allylic Carbonate **1** with Alkenylsilane **2**[a)]

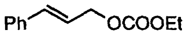
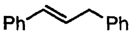
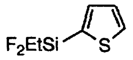
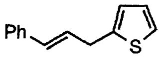
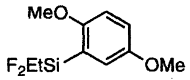
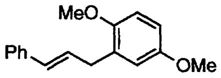
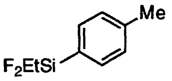
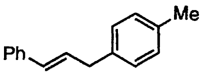
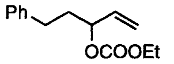
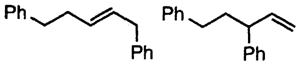
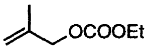
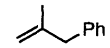
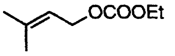
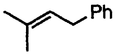
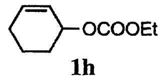
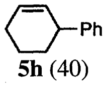
Run	Allylic carbonate	Alkenylsilane	Time (h)	Product(s) (Yield/%)[b)]
1	 **1a**	 **2a**	24	 **3a** (72)
2[c)]	**1a**	**2a**	18	**3a** (9)
3	**1a**	 **2a′**	28	**3a** (73)
4	**1a**	 **2a″**	19	No reaction
5	**1a**	 **2b**	2	 **3b** (91)
6	**1a**	 **2b′**	1	**3b** (91)
7	 **1a′**	**2b′**	1	**3b** (94)
8	 **1a″**	**2b′**	12	 (99)
9	**1a**	 **2c**	48	 **3c** (40)[e)]
10[d)]	 **1b**	 **2b′**	1.5	  **3d** + **3d′** (76, 4.4:1)[f)]
11	 **1c**	**2b′**	1	  **3e** + **3e′** (90, 3.5:1)[f)]
12	 **1d**	**2b′**	1.5	  **3f** + **3f′** (80, 2.5:1)[f)]
13	 **1e**	**2b′**	4	  **3g** + **3g′** (69, 2.0:1)[f)]

a) The reaction was carried out using alkenylsilane (2 mol equivalents), $Pd(OAc)_2$ (5 mol%), and PPh_3 (5 mol%) in DMF at 60 °C unless otherwise noted. b) Isolated yield. c) The reaction was carried out in the presence of 5 mol% of $Pd(PPh_3)_4$. d) The reaction was carried out at 90 °C. e) Recovery of **1a** was 31%. f) The ratio of **3** and **3′** was estimated by ^{1}H NMR.

fluoro)(4-methylphenyl)silane (**4d**) could be employed as the coupling partner. As before, allylic carbonates **1c**, **1f**, **1g**, and **1h** were applicable to the allyl–aryl coupling. Particularly, **1c** gave a 10 : 1 regioisomeric mixture of coupled products **5e** and **5e′**, whereas **1g** gave **5g** as the sole product.

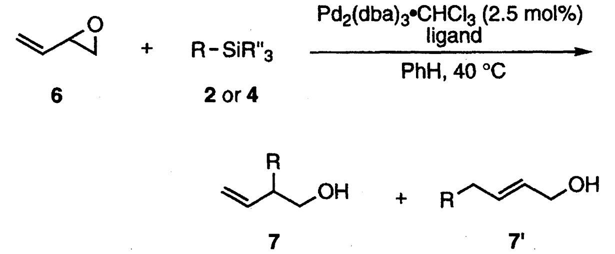
Coupling Reaction of Diene Monoxides. Based on our working hypothesis, illustrated in Scheme 4, we then examined the reaction of butadiene monoxide **6** with organosil-

Table 2. Cross-Coupling Reaction of Allylic Carbonate **1** with Arylsilane **4**[a)]

Run	Allylic carbonate	Arylsilane	Time (h)	Temp (°C)	Product(s) (Yield/%)[b)]
1	 **1a**	F_2EtSi-Ph **4a**	3	60	 **5a** (84)
2	**1a**	**4a**	4	40	**5a** (91)
3	**1a**	**4a′**	20	r.t.	**5a** (90)
4	**1a**	FMe_2Si-Ph **4a′**	12	60	**5a** (75)
5	**1a**	F_3Si-Ph **4a″**	19	60	**5a** (73)
6	**1a**	 **4b**		60	 **5b** (97)
7	**1a**	 **4c**		60	 **5c** (97)
8	**1a**	 **4d**		60	 **5d** (85)
9	 **1c**	**4a**		60	 **5e** + **5e′** (93, 10:1)[d)]
10	 **1f**	**4a**		60[c)]	 **5f** (52)
11	 **1g**	**4a**		60	 **5g** (33)
12	 **1h**	**4a**		60[c)]	 **5h** (40)

a) The reaction was carried out using arylsilane (2 mol equivalents) using $Pd_2(dba)_3 \cdot CHCl_3$ (2.5 mol%), and PPh_3 (5 mol%) in benzene unless otherwise noted. b) Isolated yield. c) The reaction was carried out in DMF. d) The ratio of **5** and **5′** was estimated by ^1H NMR.

icon compound **2** or **4**.

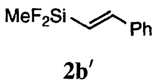
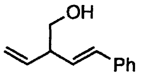
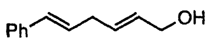
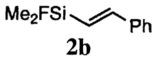
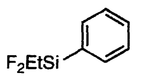
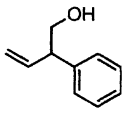
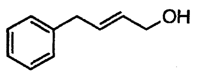
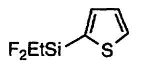
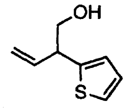
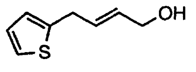
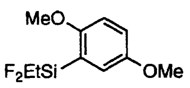
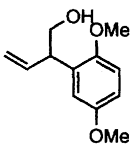
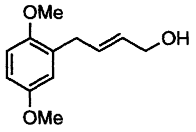
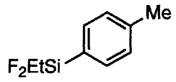
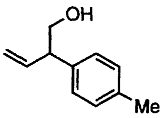
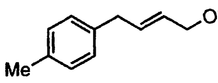


(3)

Because the coupling reaction of allylic carbonates with **2** or **4** was markedly influenced by the palladium catalyst, ligand, and solvent, we again briefly screened these factors, and found that the regioselectivity of the coupling was controllable to some extent by a proper choice of these. The results are summarized in Table 3. It is worth noting that **6** reacted at lower temperatures than allylic carbonates did. The kind of the catalyst and the molar ratio of palladium to the ligand were generally nonspecific. However, alkenylsilane **2b′** favored coupling in a 1,4-manner with $P(OCH_2)_3CEt$ as a ligand and $Pd_2(dba)_3 \cdot CHCl_3$ as a catalyst in benzene at 40 °C (Run 1), whereas a 1,2-coupling was preferred with bulky ligand $P(o\text{-}Tol)_3$ under similar conditions (Run 2). The 1,2-coupling of **2b** was switched to the 1,4-coupling using PPh_3 in DMF (Run 3). Ethyl(difluoro)phenylsilane (**4a**) also coupled with **6** to give **7b** and **7b′** in 67% yield in a ratio of 1 : 2 (Run 4). Likewise, arylsilanes **4b**, **4c**, and **4d** gave coupled products with 1,4-product being preferred.

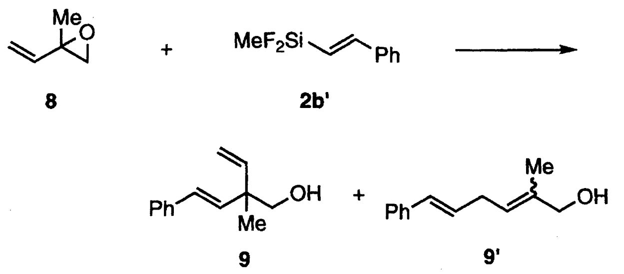
In a similar way, isoprene monoxide **8** reacted with **2b′**, giving a mixture of 1,2-coupled product **9** and 1,4-coupled product **9′**. The regioselectivity could be controlled by pro-

Table 3. Cross-Coupling Reaction of Butadiene Monoxide **6** with Alkenylsilane **2** or Arylsilane **4**[a)]

Run	R–SiR″$_3$	Ligand (mol%)	Solvent and temperature	Product(s) (Yield/%)[b)]	
1	 **2b′**	P(OCH$_2$)$_3$CEt (10)	PhH, 40 °C		 **7a** + **7a′** (59, 1 : 5.9)[c)]
2	**2b′**	P(*o*-Tol)$_3$ (10)	PhH, 40 °C		**7a** + **7a′** (55, 1.9 : 1)
3	 **2b**	PPh$_3$ (5)	DMF, 40 °C		**7a** + **7a′** (41, 1 : 4.8)[c)]
4	 **4a**	PPh$_3$ (5)	PhH, 40 °C		 **7b** + **7b′** (67, 1 : 2)
5	 **4b**	PPh$_3$ (5)	PhH, 60 °C		 **7c** + **7c′** (60, 1 : 7.1)
6	 **4c**	PPh$_3$ (5)	PhH, 60 °C		 **7d** + **7d′** (51, 1 : 1)
7	 **4d**	PPh$_3$ (5)	PhH, 60 °C		 **7e** + **7e′** (65, 1 : 2.5)

a) The reactions was carried out using **2** or **4** (2 mol equivalents) using Pd$_2$(dba)$_3$·CHCl$_3$ (2.5 mol%) and a ligand unless otherwise noted. b) Isolated yield. The ratio of **7** and **7′** was estimated by ^{1}H NMR. c) E:Z=18 : 1.

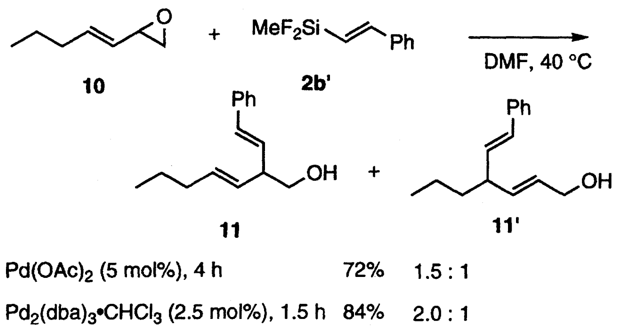
penyl choosing the catalyst, ligand, and solvent.



(4)

Table 4 lists two extreme cases: Run 1 was the best, though unsatisfactory, conditions for the production of 1,4-product **9**, and Run 2 for 1,2-product **9′**. Noteworthy is that quaternary carbogenic center in **9** was preferentially producted under the conditions of Run 2.

The regiochemistry of the coupling reaction of 1,2-epoxy-(*E*)-3-heptene (**10**) with **2b′** was studied under various conditions. In DMF at 40 °C, cross-coupled products **11** and **11′** were obtained in good yields, with 1,2-product **11** being preferred.



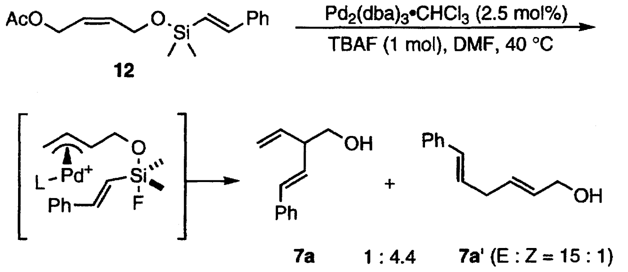
(5)

To obtain further insight into the regiochemistry of the coupling reaction of diene monoxides, we prepared allylic acetate **12** and subjected this substrate to a coupling reaction with a palladium(0) catalyst and a fluoride ion to obtain **7a** and **7a′** in a ratio of 1 : 4.4, closely related to the results of Run 3 in Table 3. Thus, the zwitter ionic intermediate shown in Eq. 6 appears to be commonly involved.

Table 4. Cross-Coupling Reactions of Isoprene Monoxide **8** with Alkenylsilane **2b′** [a)]

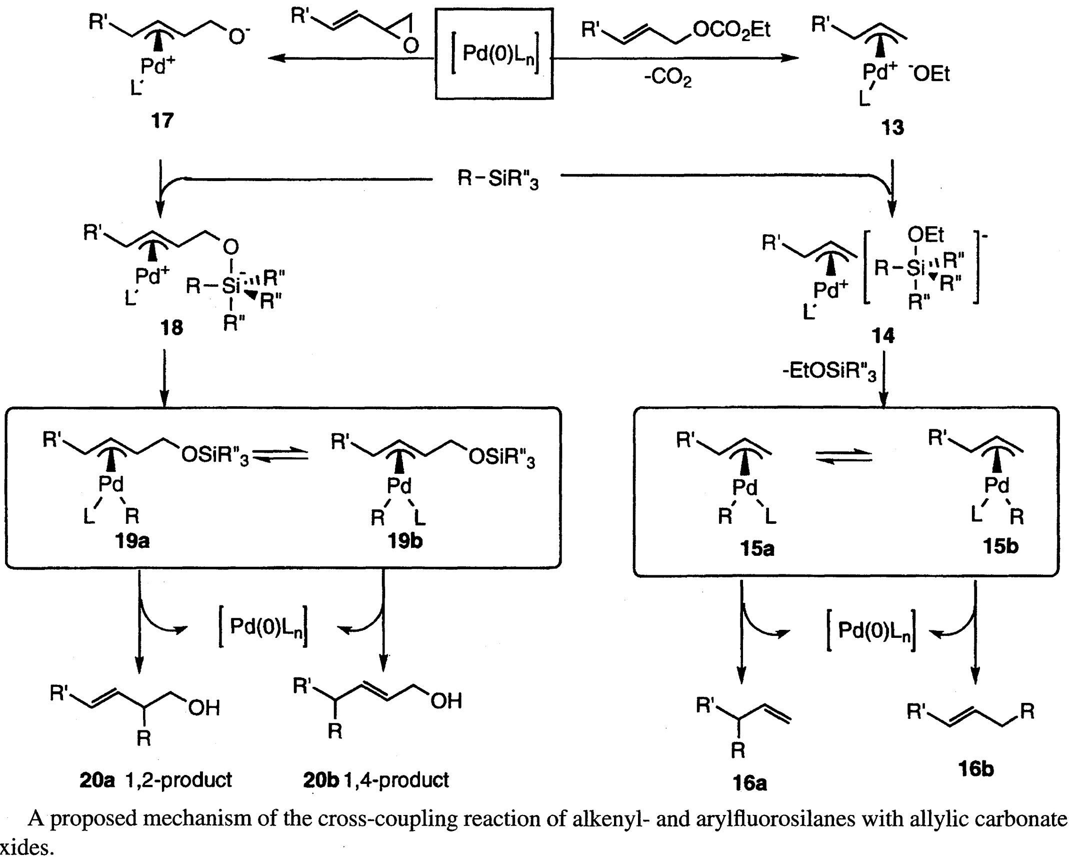
Run	Catalyst (mol%)	Ligand (mol%)	Solvent	Yield, **9** : **9′** (Isomer ratio of **9′**)[b)]
1	Pd(OAc)$_2$ (5)	PPh$_3$ (5)	DMF	45%, 1 : 4.1 (1.9 : 1)
2	Pd$_2$(dba)$_3$·CHCl$_3$(2.5)	P(*o*-Tol)$_3$ (10)	PhH	29%, 3.8 : 1 (2.0 : 1)

a) The reactions was carried out using **2b′** (2 mol equivalents) at 40 °C. b) Isolated yield. The ratio of **9** and **9′** and the isomer ratio of **9′** were estimated by ^{1}H NMR.



(6)

Mechanistic Aspects. The characteristic features of the cross-coupling reaction of allylic carbonates and diene monoxides with organosilicon compounds follow. Firstly, the reaction proceeded in the absence of a fluoride ion activator. Secondly, a coordinatively unsaturated palladium catalyst was highly effective. Thirdly, the reactivity tendency of the fluorosilyl group suitable for this coupling reaction essentially parallels that of the fluoride ion mediated cross-coupling of organosilicon compounds.[5)] Fourthly, the allylic coupling proceeded under milder conditions than those of aryl or alkenyl halides mediated by fluoride ion. Finally, most of the coupled products were obtained as regioisomeric mixtures. Based on these observations, we propose the reaction mechanism illustrated in Scheme 5. As expected, allylpalladium alkoxide **13**, produced from the reaction of Pd(0) species and an allylic carbonate through decarboxylation, should react with an organofluorosilane to provide an ion pair (**14**) of a pentacoordinate silicate anion and coordinatively unsaturated allylpalladium cationic complex. Transmetallation between the silicate anion and the allyl palladium cationic complex would give allyl(organo)palladium intermediate **15a** or **15b**. Equilibrium between these cannot be ignored, particularly when the reductive elimination leading to **16a** or **16b** proceeds at a rate comparable to, or less than, the equilibrium. The fact that regioisomeric mixtures of the products resulted might be ascribed to the relatively rapid configurational isomerization of (η^3-allyl)organopalladium complexes **15a** and **15b**.[13)] Since the equilibrium depends on the interaction between R′ and L and/or R and R′, the steric bulkiness of the phosphine ligand as well as its electronic affinity to palladium is considerably important for determin-



Scheme 5. A proposed mechanism of the cross-coupling reaction of alkenyl- and arylfluorosilanes with allylic carbonates or diene monoxides.

ing the product ratio.

The coupling reaction of a diene monoxide should proceed similarly, but intramolecularly. The catalytic cycle of the reaction should start with the oxidative addition of a Pd(0) complex to the substrate to give a zwitter ionic η^3-(alkoxy)-allylpalladium **17**, which then reacts with an organosilicon compound to afford another zwitter ionic η^3-allylpalladium silicate intermediate **18**. Intramolecular transmetallation of **18** should give at first η^3-allyl(organo)palladium **19a**. Reductive elimination of **19a** would give a 1,2-product **20a**. However, we always observed the coproduction of 1,4-product **20b**. The formation of this product can be attributed to the isomerization of **19a** to **19b** followed by reductive elimination. Thus, the configurational isomerization between **19a** and **19b** appears to take place at a rate comparable to, or faster than, that of the reductive elimination, the regioselectivity of the coupling reaction depending on the equilibrium constant between **19a** and **19b** as well as the relative rates of reductive elimination. In the reaction of butadiene monoxide **6**, the regiochemistry was also subject to the steric difference at C(1) and C(3). Indeed, a bulky ligand preferred **19a** (R′=H), giving 1,2-product **20a** predominantly, as shown in Run 2 or Table 4.

Conclusion. The palladium-catalyzed cross-coupling reaction of an allylic carbonate with an organosilicon compound is found to proceed in the absence of a fluoride ion activator. The choice of the palladium catalyst, ligand and solvent is crucial for the success of this reaction. The regioselectivity of this reaction is found to depend on the ligand employed. The reaction using a bulky phosphine ligand provided a product resulting from the coupling at a less hindered site, whereas coupling occurred at a hindered site when a cage-type phosphite was used as the ligand, which might have accelerated the reductive elimination. The reaction of diene monoxides is also achieved under mild conditions. The regioselectivity of the reaction of butadiene monoxide or isoprene monoxide with an alkenylsilane is found to be controllable by an appropriate choice of the ligand. The reaction of 1,2-epoxy-(*E*)-3-heptene (**10**) with **2b′** provides 1,2-product **11** predominantly. This observation should support the intermediacy of zwitter-ionic silicate **18**, which intramolecularly transmetallates to give **19a**, and finally **20a** as the major product.

Experimental

All of the temperatures are uncorrected. NMR spectra were measured in a $\mathrm{CDCl_3}$ solution unless otherwise noted, the chemical shifts being given in ppm. ^{1}H NMR spectra (tetramethylsilane as an internal standard) were measured on a JEOL EX-400 or Bruker AC-200 spectrometer. ^{13}C NMR spectra ($\mathrm{CDCl_3}$ as an internal standard) were measured on a JEOL EX-400 or Bruker AC-200 spectrometer. IR spectra were recorded with a Shimadzu FTIR-8000A spectrometer in neat, unless otherwise noted. Mass spectra were recorded with a Hitachi M-80 spectrometer or a Shimadzu QP-5000 GC-MS system. Elemental analyses were carried out by Elemental Analysis Center, Tokyo Institute of Technology, using Yanako MT2 CHN Corder.

All of the reactions were carried out under an argon atmosphere, unless otherwise noted. Diethyl ether, THF, and benzene were distilled from sodium/benzophenone prior to use. Hexane and pentane were distilled from sodium/benzophenone and stored over MS-4A under an argon atmosphere. Dichloromethane, DMF, DMSO, DMI, and HMPA were distilled from $\mathrm{CaH_2}$ and stored over MS-4A under an argon atmosphere.

Column chromatography was performed using Merck Kieselgel 60 (70—230 mesh) or Wakogel C-200. Flash column chromatography was performed using Merck Kieselgel 60 (230—400 mesh). Palladium catalysts $\mathrm{Pd(PPh_3)_4}$ [14] and $\mathrm{Pd_2(dba)_3 \cdot CHCl_3}$ [15] were prepared according to the corresponding literature. Triphenylphosphine and P(*o*-Tol)$_3$ were purchased from Tokyo Kasei Kogyo and purified by recrystalization from hexane.

Alkenylfluorosilane **2** was prepared by hydrosilylation of the corresponding alkyne with $\mathrm{HSiMeCl_2}$ or $\mathrm{HSiMe_2Cl}$ using a $(n\text{-}\mathrm{Bu_4N})_2\mathrm{PtCl_6}$ [16] catalyst followed by fluorination with $\mathrm{CuF_2 \cdot 2H_2O}$.[17] Commercially available arylsilanes were purchased. Those unavailable were prepared according to the reported procedures.[5]

A General Procedure for the Preparation of Allylic Carbonates: The corresponding chloroformate (12 mmol) was added dropwise to a solution of an allylic alcohol (10 mmol) dissolved in dichloromethane (10 ml) and pyridine (2 ml) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred until all of the allylic alcohol was consumed, and then treated with a saturated ammonium chloride aqueous solution. The organic layer was separated, and the aqueous layer was extracted twice with diethyl ether. The combined organic layer was washed with water and dried over anhydrous sodium sulfate. Concentration under reduced pressure followed by purification by flash column chromatography on silica gel or by vacuum distillation gave the desired carbonates. Analytical and spectroscopic properties of the products are shown below, except for **1a**,[18] **1d**,[19] **1f**,[18] and **1h**.[20]

Isopropyl (*E*)-3-Phenyl-2-propenyl Carbonate (1a′). ^{1}H NMR (200 MHz) δ=1.31 (d, J=6.0 Hz, 6H), 4.77 (dd, J=6.5, 1.3 Hz, 2H), 4.90 (hept, J=6.0 Hz, 1H), 6.29, (dt, J=16.0, 6.5 Hz, 1H), 6.69 (brd, J=16.0 Hz, 1H), 7.21—7.42 (m, 5H); ^{13}C NMR (50.3 MHz) δ=21.8, 68.0, 72.0, 122.7, 126.7, 128.1, 128.6, 134.6, 136.1, 154.5; IR 3084, 3061, 3029, 2984, 2942, 2880, 1740, 1468, 1296, 1111, 968, 925, 910, 824, 793, 749, 693 cm^{-1}. Found; *m/z* 220.1083. Calcd for $\mathrm{C_{13}H_{16}O_3}$: M, 220.1099.

Phenyl (*E*)-3-Phenyl-2-propenyl Carbonate (1a″). ^{1}H NMR (200 MHz) δ=4.89 (dd, J=6.5, 1.0 Hz, 2H), 6.35, (dt, J=16.0, 6.5 Hz, 1H), 6.75 (d, J=16.0 Hz, 1H), 7.16—7.44 (m, 10H); ^{13}C NMR (50.3 MHz) δ=69.0, 120.9, 121.8, 125.4, 126.7, 128.2, 128.6, 129.4, 129.5, 135.3, 135.8, 151.1, 153.5; IR 3061, 3029, 1755, 1593, 1580, 1495, 1300, 1213, 986, 974, 814, 779 cm^{-1}. Found: *m/z* 254.0939. Calcd for $\mathrm{C_{16}H_{14}O_3}$: M, 254.0939.

Ethyl 1-Methyl-2-propenyl Carbonate (1b). ^{1}H NMR (200 MHz) δ=1.31 (t, J=7.5 Hz, 3H), 1.37 (d, J=7.5 Hz, 3H), 4.19, (q, J=7.5 Hz, 2H), 5.11—5.34 (m, 3H), 5.87 (ddd, J=16.0, 10.0, 6.0 Hz, 1H); ^{13}C NMR (50.3 MHz) δ=14.2, 20.0, 63.8, 74.9, 116.4, 137.2, 154.5; IR 3090, 2986, 2938, 1764, 1374, 1260, 1090, 932, 907, 884, 791 cm^{-1}. Found: *m/z* 144.0803. Calcd for $\mathrm{C_7H_{12}O_3}$: M, 144.0786.

Ethyl 1-(2-Phenylethyl)-2-propenyl Carbonate (1c). ^{1}H NMR (200 MHz) δ=1.32 (t, J=7.0 Hz, 3H), 1.83—2.17 (m, 2H), 2.58—2.81 (m, 2H), 4.19, (q, J=7.0 Hz, 2H), 5.08 (brq, J=7.0 Hz, 1H), 5.23 (brq, J=10.0 Hz, 1H), 5.32 (brd, J=16.0 Hz, 1H), 5.84 (ddd, J=16.0, 10.0, 7.0 Hz, 1H), 7.14—7.33 (m, 5H); ^{13}C NMR (50.3 MHz) δ=31.3, 25.9, 63.9, 78.2, 117.7, 126.0, 128.3, 128.4, 135.8, 141.1, 154.6; IR 3086, 3065, 3029, 2986, 2864, 1744, 1647, 1605, 1497, 1456, 1372, 1260, 1094, 1009, 939, 791, 750, 700 cm^{-1}. Found: *m*/*z* 234.1253. Calcd for $C_{14}H_{18}O_3$: M, 234.1256.

Ethyl (*Z*)-4-*t*-Butyldimethylsilyloxy-2-butenyl Carbonate (1e). ^{1}H NMR (200 MHz) δ=0.10 (s, 6H), 0.91 (s, 9H), 1.31 (t, J=7.0 Hz, 3H), 4.20 (q, J=7.0 Hz, 2H), 4.28 (ddt, J=6.0, 1.5, 1.0 Hz, 2H), 4.71 (ddt, J=6.5, 1.0, 1.0 Hz, 2H), 5.59 (dtt, J=16.5, 6.5, 1.0 Hz, 1H), 5.76 (dtt, J=16.5, 6.0, 1.0 Hz, 1H); ^{13}C NMR (50.3 MHz) δ=−5.3, 14.2, 18.3, 25.9, 59.5, 63.6, 64.0, 123.7, 134.4, 155.1; IR 2957, 2932, 2859, 1748, 1472, 1258, 1090, 839, 777 cm^{-1}. Found: *m*/*z* 260.1461. Calcd for $C_{12}H_{24}O_4Si$: M, 260.1444.

Ethyl 3-Methyl-2-butenyl Carbonate (1g). ^{1}H NMR (200 MHz) δ=1.30, (t, J=7.0 Hz, 3H), 1.73 (s, 3H), 1.76 (s, 3H), 4.19 (q, J=7.0 Hz, 2H), 4.62 (d, J=8.0 Hz, 2H), 5.38 (mt, J=8.0 Hz, 1H); ^{13}C NMR (50.3 MHz) δ=14.3, 18.0, 25.7, 63.4, 64.4, 118.1, 139.9, 155.3; IR 2984, 2940, 2917, 1744, 1676, 1449, 1379, 1335, 1252, 1007, 916, 876, 793 cm^{-1}. Found: *m*/*z* 158.0942. Calcd for $C_8H_{14}O_3$: M, 158.0943.

A General Procedure for the Cross-Coupling Reaction of Allylic Carbonates with Organofluorosilanes: A mixture of a palladium catalyst (2.5 to 5 mol%) and a phosphine ligand (up to 10 mol%) in a solvent (1 ml) was stirred for 10—30 min at room temperature in a screw capped glass tube. An allylic carbonate (0.40 mmol) and an organosilicon compound (0.80 mmol) were added to the mixture, and the whole reaction mixture was stirred at the specified temperature. The reaction was monitored by TLC. After all of the carbonate was consumed, the solvent was removed under vacuum, and the residue was purified briefly by column chromatography (silica gel, hexane–ethyl acetate 10 : 1) to remove the palladium catalyst. The product was further purified by flash column chromatography on silica gel. Spectroscopic data of (*E*,*E*)-1-phenyl-1,4-undecadiene (**3a**),[21] (*E*)-1-phenyl-3-(2-thienyl)propene (**5b**),[22] (*E*)-3-(4-methylphenyl)-1-phenylpropene (**5d**),[23] 2-methyl-3-phenylpropene (**5f**),[24] 2-methyl-4-phenyl-2-butene (**5g**),[24] and 3-phenylcyclohexene (**5h**)[25] were compared with the reported ones. Following products were characterized analytically and/or spectrometrically.

1,5-Diphenyl-1,4-pentadiene (3b). ^{1}H NMR (200 MHz) δ=3.13 (tt, J=6.5, 1.0 Hz, 2H), 6.29 (dd, J=16.0, 6.5 Hz, 2H), 6.48 (br d, J=16.0 Hz, 2H), 7.20—7.42 (m, 10H); ^{13}C NMR (50.3 MHz) δ=36.18, 126.05, 127.03, 128.17, 128.50, 130.99, 137.52; IR 3027, 1495, 1447, 965, 741, 693 cm^{-1}. Found: C, 92.78; H, 7.28%. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32%.

(*E*,*E*)-1-Phenyl-4-propyl-1,4-octadiene (3c). ^{1}H NMR (200 MHz) δ=0.91 (t, J=7.0 Hz, 3H), 0.91 (t, J=7.0 Hz, 3H), 1.39 (m, 4H), 2.03 (m, 4H), 2.88 (dt, J=7.0, 1.0 Hz, 2H), 5.23 (t, J=7.0 Hz, 1H), 6.19 (dt, J=7.0, 15.5 Hz, 1H), 6.39 (br d, J=15.5 Hz, 1H), 7.30 (m, 5H); ^{13}C NMR (50.3 MHz) δ=13.9, 14.1, 21.5, 23.2, 30.0, 32.3, 40.6, 126.0, 126.5, 126.8, 128.5, 129.6, 130.7, 137.8, 137.9; IR 3083, 3061, 3027, 2959, 2930, 2870, 1599, 1497, 1377, 965, 747 cm^{-1}. Found: *m*/*z* 228.1876. Calcd for $C_{17}H_{24}$: M, 228.1878.

(*E*,*E*)-1-Phenyl-1,4-hexadiene (3d)[26] **and (*E*)-3-Methyl-1-phenyl-1,4-pentadiene (3d′).**[27] The products were obtained as an inseparable mixture. The ratio was determined by ^{1}H NMR (200 MHz) δ=1.68 (m, 3H) for **3d** and δ=1.06 (d, J=7.0 Hz, 3H) for **3d′**. Found: C, 92.65; H, 7.16%. Calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26%.

(*E*,*E*)-1,7-Diphenyl-1,4-heptadiene (3e) and (*E*)-3-Ethenyl-1,5-diphenyl-1-pentene (3e′). These were obtained as an inseparable mixture. The ratio of **3e** : **3e′** was determined by ^{1}H NMR (200 MHz).

3e: δ=1.83 (m, 2H), 2.67 (t, J=6.0 Hz, 2H), 2.94 (m, 1H), 5.09 (ddd, J=10.0, 1.0, 1.0 Hz, 1H), 5.10 (ddd, J=17.0, 1.5, 1.0 Hz, 1H), 5.84, (ddd, J=17.0, 10.0, 7.0 Hz, 1H), 6.08 (dt, J=16.0, 8.0 Hz, 1H), 6.41 (d, J=16.0 Hz, 1H), 7.20—7.40 (m, 10H).

3e′: δ=2.36 (m, 2H), 2.70 (dt, J=7.5 Hz, 2H), 2.90 (m, 2H), 5.51 (dt, J=15.5, 5.0 Hz, 1H), 5.60 (dt, J=15.5, 5.5 Hz, 1H), 6.19 (dt, J=16.0, 6.5 Hz, 1H), 6.36 (d, J=16.0 Hz, 1H), 7.18—7.40 (m, 10H). Found (as a mixture): *m*/*z* 248.1571. Calcd for $C_{19}H_{20}$: M, 248.1565.

(*E*,*E*)-6-Benzyloxy-1-phenyl-1,4-hexadiene (3f) and (*E*)-3-Benzyloxymethyl-1-phenyl-1,4-pentadiene (3f′). Following ^{1}H NMR (200 MHz) signals were assigned to **3f**: δ=2.98 (m, 2H), 4.02 (m, 2H), 4.53 (s, 2H), 5.69 (dtt, J=15.5, 5.5, 1.0 Hz, 1H), 5.83 (dtt, J=16.0, 6.0, 1.0 Hz, 1H), 6.21 (dt, J=15.5, 6.5 Hz, 1H), 6.42 (br d, J=15.5 Hz, 1H), 7.20—7.39 (m, 10H).

3f′: δ=3.27 (m, 1H), 3.56 (d, J=6.5 Hz, 2H), 4.57 (s, 2H), 5.15 (dt, J=11.0, 1.0 Hz, 1H), 5.17 (dt, J=16.5, 1.0 Hz, 1H), 5.91 (m, 1H), 6.19 (dd, J=7.5, 16.0 Hz, 1H), 6.46 (d, J=16.0 Hz, 1H), 7.16—7.40 (m, 10H). Found (as a mixture): *m*/*z* 264.1510. Calcd for $C_{19}H_{20}O$: M, 264.1514.

(*E*,*E*)-6-(*t*-Butyldimethylsilyl)oxy-1-phenyl-1,4-hexadiene (3g) and (*E*)-3-(*t*-Butyldimethylsilyl)oxymethyl-1-phenyl-1,4-pentadiene (3g′). Each product was separated by column chromatography on silica gel.

3g: ^{1}H NMR (200 MHz) δ=0.08 (s, 6H), 0.92 (s, 9H), 2.95 (m, 2H), 4.17 (m, 2H), 5.63 (dtt, J=15.5, 4.5, 1.0 Hz, 1H), 5.75 (ddt, J=15.5, 6.0, 1.0 Hz, 1H), 6.22 (dt, J=16.0, 6.0 Hz, 1H), 6.41 (d, J=16.0 Hz, 1H), 7.18 —7.39 (m, 5H); ^{13}C NMR (50.3 MHz) δ=−5.13, 18.43, 25.99, 35.46, 63.81, 126.00, 126.96, 128.46, 128.49, 128.51, 130.63, 130.66, 137.64; IR 2955, 2930, 2857, 1256, 967, 835, 776 cm^{-1}. Found: C, 74.98; H, 10.05%. Calcd for $C_{18}H_{28}OSi$: C, 74.98; H, 9.78%.

3g′: ^{1}H NMR (200 MHz) δ=0.05 (s, 3H), 0.06 (s, 3H), 0.90 (s, 9H), 3.09 (m, 1H), 3.68 (d, J=6.5 Hz, 2H), 5.13 (m, 1H), 5.14 (m, 1H), 5.90 (m, 1H), 6.19 (dd, J=7.0, 16.0 Hz, 1H), 6.44 (d, J=16.0 Hz, 1H), 7.18—7.40 (m, 5H); ^{13}C NMR (50.3 MHz) δ=−5.28, −5.27, 18.35, 25.91, 49.68, 66.42, 116.00, 126.11, 127.07, 128.47, 129.87, 131.13, 137.63, 138.21; IR 2955, 2930, 2857, 1256, 1105, 965, 916, 837, 776 cm^{-1}. Found: C, 74.98; H, 10.05%. Calcd for $C_{18}H_{28}OSi$: C, 74.98; H, 9.78%.

(*E*)-1,3-Diphenylpropene (5a). ^{1}H NMR (200 MHz) δ=3.56 (d, J=6.0 Hz, 2H), 6.36 (dt, J=6.0 Hz, 15.5 Hz, 1H), 6.48 (d, J=15.5 Hz, 1H), 7.16—7.40 (m, 10H); ^{13}C NMR (50.3 MHz) δ=39.3, 126.1, 126.2, 127.1, 128.5, 128.6, 129.2, 131.1, 137.5, 140.1; IR 3104, 3083, 3027, 2897, 2832, 1946, 1875, 1804, 1750, 1701, 1601, 1495, 1153, 1105, 1075, 982, 789, 739 cm^{-1}. Found: C, 92.65; H, 7.16%. Calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26%.

(*E*)-3-(2,5-Dimethoxyphenyl)-1-phenylpropene (5c). ^{1}H NMR (200 MHz) δ=3.51 (d, J=6.0 Hz, 2H), 3.75 (s, 3H), 3.80 (s, 3H), 6.36 (dt, J=6.0 Hz, 15.5 Hz, 1H), 6.48 (d, J=15.5 Hz, 1H), 6.69—6.82 (m, 3H), 7.13—7.37 (m, 5H); ^{13}C NMR (50.3 MHz) δ=33.5, 55.7, 56.1, 111.3, 111.5, 116.3, 126.1, 126.9, 128.4, 128.6, 130.0, 130.9, 137.7, 151.6, 153.6; IR 3060, 3027, 3000, 2948, 2907, 2833, 1592, 1499, 1225, 1048, 799, 743 cm^{-1}. Found: *m*/*z* 254.1306. Calcd for $C_{17}H_{18}O_2$: M, 254.1307.

(*E*)-1,5-Diphenyl-2-pentene (5e)[28] **and 3,5-Diphenyl-1-pentene (5e′).**[29] These were obtained as an inseparable mixture. The ratio was determined by ^{1}H NMR (200 MHz) δ=3.32 (d, J=8 Hz, 2H) for **5e** and δ=5.04 (brs, 1H) for **5e′**.

Cross-Coupling Reaction of a Diene Monoxide with an Organosilicon Compound. A General Procedure. A mixture of a palladium catalyst (2.5 to 5 mol%) and a phosphine ligand (up to 10 mol%) in a solvent (1 ml) was stirred for 10—30 min at room temperature in a screw-capped glass tube. A diene monoxide

(0.40 mmol) and an organosilicon compound (0.80 mmol) were added to the mixture and the resulting mixture was stirred at 40 °C until all of the diene monoxide was consumed. A workup followed by column chromatography (silica gel, hexane–ethyl acetate 4 : 1) gave a crude product, which was further purified by flash column chromatography on silica gel.

(*E*)-2-Ethenyl-4-phenyl-3-buten-1-ol (7a).[30] ^{1}H NMR (200 MHz) δ=3.14 (ddt, J=7.0, 7.0, 7.0 Hz, 1H), 3.66 (t, J=6.5 Hz, 1H), 5.22 (ddd, J=10.5, 1.0, 1.0 Hz, 1H), 5.22 (ddd, J=17.5, 1.5, 1.5 Hz, 1H), 5.84 (ddd, J=17.5, 10.0, 7.0 Hz, 1H), 6.13 (dd, J=16.0, 7.5 Hz, 1H), 6.51 (d, J=16.0 Hz, 1H), 7.20—7.40 (m, 5H); ^{13}C NMR (200 MHz) δ=49.99, 65.20, 117.24, 126.19, 127.46, 128.53, 128.55, 132.22, 137.01, 137.33; IR 3370, 3027, 1599, 1495, 1448, 1048, 968, 918, 749, 693 cm^{-1}.

(*E*,*E*)-6-Phenyl-2,5-hexadien-1-ol (7a′).[30] ^{1}H NMR (200 MHz) δ=2.96 (m, 2H), 4.13 (br d, J=4 Hz, 2H), 5.72 (dt, J=15.5, 4.5 Hz, 1H), 5.81 (dt, J=15.5, 5.0 Hz, 1H), 6.20 (dt, J=16.0, 6.5 Hz, 1H), 6.41 (d, J=16.0 Hz, 1H), 7.15—7.38 (m, 5H); ^{13}C NMR (50.3 MHz) δ=35.45, 63.53, 126.00, 127.05, 128.00, 128.47, 130.24, 130.92, 137.48; IR 3330, 3027, 2870, 1597, 1495, 1449, 1426, 1089, 968, 912, 745, 693 cm^{-1}.

2-Phenyl-3-buten-1-ol (7b).[30] ^{1}H NMR (200 MHz) δ=3.52 (dt, J=7.0, 7.0 Hz, 1H), 3.82 (m, 2H), 5.18 (ddd, J=17.0, 1.5, 1.5 Hz, 1H), 5.21 (ddd, J=10.5, 1.5, 1.5 Hz, 1H), 6.01 (ddd, J=17.0, 10.5, 7.5 Hz, 1H), 7.20—7.36 (m, 5H); ^{13}C NMR (50.3 MHz) δ=52.49, 66.04, 117.03, 126.91, 127.93, 128.72, 138.21, 140.60; IR 3360, 3029, 2876, 1638, 1601, 1493, 1055, 995, 920, 758, 700 cm^{-1}.

(*E*)-4-Phenyl-2-buten-1-ol (7b′).[30] ^{1}H NMR (200 MHz) δ=1.33 (br, 1H), 3.39 (d, J=6.0 Hz, 2H), 4.11 (br d, J=6.0 Hz, 2H), 5.62—5.95 (m, 2H), 7.16—7.34 (m, 5H); ^{13}C NMR (50.3 MHz) δ=38.6, 63.5, 126.1, 128.4, 128.5, 130.3, 131.5, 140.0; IR 3330 (br), 3085, 3063, 3027, 2869, 1670, 1603, 1495, 1453, 999, 972, 747, 698 cm^{-1}.

2-(2-Thienyl)-3-butene-1-ol (7c) and (*E*)-4-(2-Thienyl)-2-buten-1-ol (7c′). The products were obtained as an inseparable mixture, the ratio being determined by ^{1}H NMR (200 MHz).

7c: δ=3.82 (br, 3H), 5.20—5.29 (m, 2H), 5.90—6.07 (m, 1H), 6.79—6.82 (m, 1H), 6.99 (dd, J=3.5, 5.1 Hz, 1H), 7.22 (dd, J=1.2, 5.1 Hz, 1H).

7c′: δ=3.58 (d, J=6.0 Hz, 2H), 4.14 (d, J=4.7 Hz, 2H), 6.79—6.82 (m, 1H), 6.93 (dd, J=3.4, 5.2 Hz, 1H), 7.14 (dd, J=1.3, 5.2 Hz). Found (as a mixture): m/z 154.0435. Calcd for $C_8H_{10}OS$: M, 154.0452.

2-(2,5-Dimethoxyphenyl)-3-buten-1-ol (7d) and (*E*)-4-(2,5-Dimethoxyphenyl)-2-buten-1-ol (7d′). The products were obtained as an inseparable mixture, whose ratio was determined by ^{1}H NMR.

7d: ^{1}H NMR (200 MHz) δ=1.60 (br 1H), 3.74—3.89 (m, 8H), 3.90—4.01 (m, 1H), 5.15—5.24 (m, 2H), 5.96—6.13 (m, 2H), 6.69—6.85 (m, 3H).

7d′: ^{1}H NMR (200 MHz) δ=3.35 (d, J=6.0 Hz, 2H), 3.75 (s, 3H), 3.78 (s, 3H), 4.10 (dd, J=5.5, 1.0 Hz, 2H), 5.60—5.96 (m, 2H), 6.67—6.85 (m, 3H). Found (as a mixture): m/z 208.1108. Calcd for $C_{12}H_{16}O_3$: M, 208.1099.

2-(4-Methylphenyl)-3-buten-1-ol (7e).[31] ^{1}H NMR (200 MHz) δ=2.32 (s, 3H), 3.49 (dd, J=7.4, 14.3 Hz, 1H), 3.80 (m, 2H), 5.17 (ddd, J=1.6, 1.6, 16.6 Hz), 5.20 (ddd, J=1.2, 1.8, 10.9 Hz), 5.99 (ddd, J=7.6, 10.9, 16.6 Hz), 7.09—7.18 (m, 4H).

(*E*)-4-(4-Methylphenyl)-2-buten-1-ol (7e′).[31] ^{1}H NMR (200 MHz) δ=2.32 (s, 3H), 3.34 (d, J=6.4 Hz, 2H), 4.12 (dd, J=7.0, 7.0 Hz, 2H), 5.61—5.94 (m, 2H), 7.04—7.13 (m, 4H).

(*E*)-2-Ethenyl-2-methyl-4-phenyl-3-buten-1-ol (9).[30] ^{1}H NMR (200 MHz) δ=1.25 (s, 3H), 3.55 (d, J=6.5 Hz, 2H), 5.17 (dd, J=17.5, 1.0 Hz, 1H), 5.22 (dd, J=11.0, 1.0 Hz, 1H), 5.92 (dd, J=17.5, 1.0 Hz, 1H), 6.21 (d, J=16.5 Hz, 1H), 6.46 (d, J=16.0 Hz, 1H), 7.17—7.41 (m, 5H); ^{13}C NMR (50.3 MHz) δ=20.94, 45.44, 69.60, 114.93, 126.20, 127.37, 128.53, 129.76, 133.95, 137.23, 142.42; IR 3390, 3083, 2932, 1495, 1449, 1042, 970, 918, 747, 692 cm^{-1}.

(5*E*)-2-Methyl-6-phenyl-2,5-hexadien-1-ol (9′).[30] Obtained as an inseparable mixture of (2*E*)- and (2*Z*)-isomers. Major product exhibited ^{1}H NMR (200 MHz) δ=1.73 (s, 3H), 2.97 (dd, J=6.5, 6.5 Hz, 2H), 4.05 (br s, 2H), 5.53 (tq, J=7.5, 1.5 Hz, 1H), 6.18 (dt, J=16.0, 6.0 Hz, 1H), 6.40 (d, J=16.0 Hz, 1H), 7.15—7.35 (m, 5H) and assigned as the (2*E*)-isomer based on the long range allylic coupling between CH_3 and the olefinic methine proton. Minor isomer showed ^{1}H NMR (200 MHz) δ=1.85 (q, J=1.0 Hz, 3H), 2.96 (dd, J=6.5, 6.5 Hz, 2H), 4.18 (br s, 2H), 5.42 (t, J=7.5 Hz, 1H), 6.17 (dt, J=16.0, 6.0 Hz, 1H), 6.39 (d, J=16.0 Hz, 1H), 7.15—7.35 (m, 5H) and assigned as the (2*Z*)-isomer.

(*E*,*E*)-2-(2-Phenylethenyl)-3-hepten-1-ol (11) and (*E*,*E*)-4-(2-Phenylethenyl)-2-hepten-1-ol (11′).[30] The products were obtained as an inseparable mixture, the ratio being determined by ^{1}H NMR (200 MHz).

11: δ=0.92 (t, J=7.0 Hz, 3H), 1.43 (td, J=7.5, 7.0 Hz, 2H), 2.06 (ddt, J=7.0, 7.0, 1.0 Hz, 2H), 3.09 (dt, J=7.0, 7.0 Hz, 1H), 3.61 (m, 2H), 5.41 (ddt, J=16.0, 7.0, 1.0 Hz, 1H), 5.67 (ddt, J=15.5, 6.5, 1.0 Hz, 1H), 6.13 (dd, J=16.5, 7.5 Hz, 1H), 6.49 (dd, J=16.0, 1.0 Hz), 7.18—7.41 (m, 5H).

11′: δ=0.92 (t, J=7.0 Hz, 3H), 1.27—1.55 (m, 4H), 2.90 (m, 1H), 4.14 (brs, 2H), 5.69 (m, 2H), 6.09 (dd, J=16.0, 8.0 Hz, 1H), 6.37 (d, J=16.0 Hz, 1H), 7.15—7.35 (m, 5H). Found (as a mixture): m/z 216.1524. Calcd for $C_{15}H_{20}O$: M, 216.1514.

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