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STEREOSELECTIVE PREPARATION OF 1,4-DIENES BY PALLADIUM CATALYZED ALLYLATION OF (*E*)-ALKENYLPENTAFLUOROSILICATES.[1] APPLICATION TO TOTAL SYNTHESIS OF (±)-RECIFEIOLIDE

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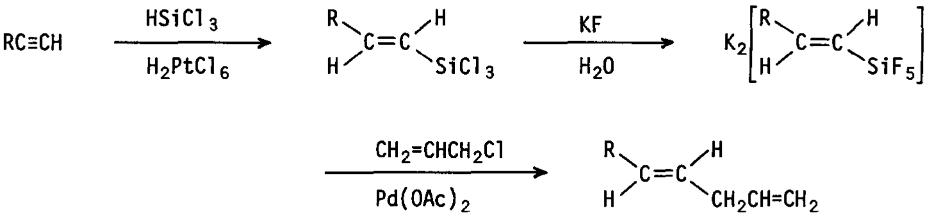
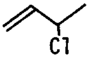
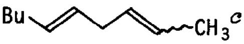
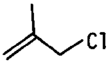
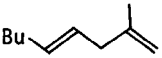
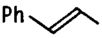
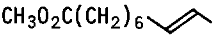
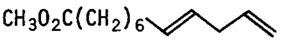
The formation of carbon-carbon bonds is one of the most fundamental problems in organic chemistry and numerous selective reactions have been explored by transition metal catalysis.[2] We recently have shown that organopentafluorosilicates are potentially useful intermediates in organic synthesis for preparing carbon-halogen and -oxygen bonds.[3] However, these compounds have scarcely been employed as effective reagents for the carbon-carbon bond formation.[4] We have now found that alkenylpentafluorosilicates derived from terminal acetylenes readily react with allylic substrates under the influence of palladium salts to provide the cross-coupling product, 1,4-dienes, in good yields (Table 1).



Hydrosilylation of terminal acetylenes catalyzed by chloroplatinic acid proceeds readily to give the terminal alkenylsilanes mainly and the internal adducts as minor products (95 : 5 at 5°C).[5] The *E* stereochemistry (cis addition) of the former has been well established[5] and in the allyl-coupling product no loss of the stereochemistry was confirmed by GLC, ^{1}H NMR, and IR.[6] It is also of interest to note that no coupling product was detected from the internal isomer and therefore the olefin obtained was completely regio- and stereo-isomerically pure. Thus, the present procedure provides a new regio- and stereo-selective transformation of acetylenes into

Table 1. Cross-Coupling Reaction of Alkenylsilicates with Allylic Halides[a]

R in $K_2[RSiF_5]$	Allylic substrate	Equiv	Catalyst	Solvent	Product	Yield[b] (%)
		1.0	$Pd(OAc)_2$	Et_2O		38
		2.0		Et_2O		60
		5.0		Et_2O		66
		10.0		Et_2O		69
		10.0		THF		71
		10.0		CH_3CN		50
		10.0		C_6H_6		50
		10.0	$PdCl_2$	THF		39
		10.0	$Pd(acac)_2$	THF		trace
		10.0	$Pd(OAc)_2$	THF		60
		10.0		THF		4
		10.0		THF	 [c]	59
		10.0		THF		35[d]
		10.0		THF		40[e]
		10.0		THF		55[f]

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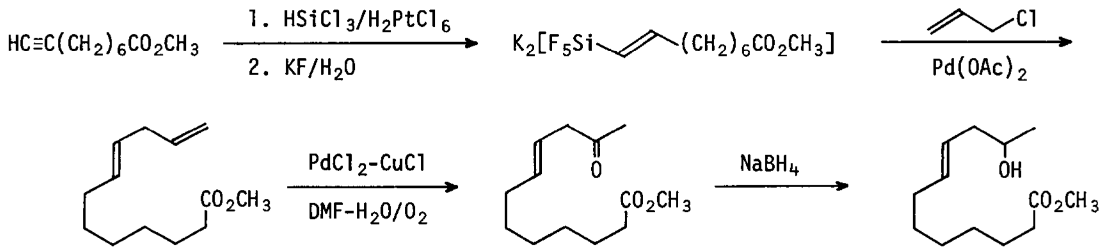
[a] Unless otherwise noted, the reaction was carried out for 24 h at room temperature in the presence of 10 mol% of a catalyst. [b] Determined by GLC. [c] A mixture of (2*E*,5*E*)- and (2*Z*,5*E*)-2,5-decadiene was obtained. [d] Refluxed for 4 h. [e] For 7 h. [f] Isolated yield.

(*E*)-1,4-dienes.[7] Another significant feature is that the present procedure is capable of tolerating some functional groups such as an ester group which, in most cases, is incompatible with hydroalumination.[7b]

Although the scope of the present reaction has not been fully explored, several allylic halides, such as allyl chloride, allyl bromide, methallyl chloride, and 3-chloro-1-butene, were found to be effective as an allylic substrate. Allyl acetate was almost ineffective. In the reaction with 3-chloro-1-butene the carbon-carbon bond formation occurred at the γ position exclusively, in accord with the mechanism involving addition of an alkenyl-palladium intermediate[8] across the double bond of an allylic halide followed by elimination of palladium chloride species.[9] As a catalyst palladium acetate was more effective than palladium chloride. Palladium acetylacetonate was almost inactive. THF was the most suitable solvent and the use of 10 equivalents of an allylic halide was most satisfactory.

The simplicity of the present procedure is illustrated by the following example. $K_2[(E)\text{-BuCH=CHSiF}_5]$ (1.422 g; 5.0 mmol), allyl chloride (4.10 mL; 50 mmol), palladium acetate (112 mg; 0.50 mmol), and dry THF (10 mL) were combined, and stirred at room temperature for 24 h. After the addition of pentane (20 mL) insoluble matters were filtered and the solvent was evaporated. The residue was distilled to give 259 mg of (*E*)-1,4-nonadiene (42% yield).

To illustrate one of the unique synthetic applications of the present coupling reaction, we have developed a new route to methyl (±)-11-hydroxy-*trans*-8-dodecenoate,[10] a precursor of recifeiolide, the naturally occurring macrolide from cephlosporium recifei.[11]



A silicate, $K_2[F_5SiCH{=}CH(CH_2)_6CO_2CH_3]$, prepared by hydrosilylation of methyl 8-nonynoate[12] followed by treatment with aqueous potassium fluoride (62% yield), was allowed to react with allyl chloride in the presence of palladium acetate as above. Methyl *trans*-8,11-dodecadienoate obtained (55% yield) was oxidized by the Wacker process ($PdCl_2$-$CuCl$/DMF-H_2O/O_2 system)[13] to give methyl 11-oxo-*trans*-8-dodecenoate in 67% yield. Reduction with $NaBH_4$ gave isomerically pure methyl (±)-11-hydroxy-*trans*-8-dodecenoate in 93% yield: IR (film); 3410 (br), 1748, 965 cm^{-1}. ^1H NMR (CCl_4); δ 1.10 (d, 3H, J=6.5), 1.0-1.8 (m, 8H), 1.8-2.2 (m, 4H), 2.20 (t, 2H, J=8.0), 3.59 (s, 3H), 3.5-3.8 (m, 1H), 5.3-5.5 (m, 2H). MS; 210 (4.6%), 184 (16.4%), 152 (53.4%), 84 (100%). Anal. Found; C 68.61, H 10.53. Calcd for $C_{13}H_{24}O_3$; C 63.38, H 10.59.

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