

Silylation and alkylation of allenes using chlorosilanes and alkyl halides in the presence of palladium catalyst and Grignard reagents

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Abstract

Allenes react with Grignard reagents and chlorosilanes in the presence of a palladium catalyst giving rise to carbosilylated products bearing carbon groups from Grignard reagents at the central carbon and silyl groups at the terminal carbon. When alkyl halides were used instead of chlorosilanes, the corresponding alkylated products were obtained.

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1. Introduction

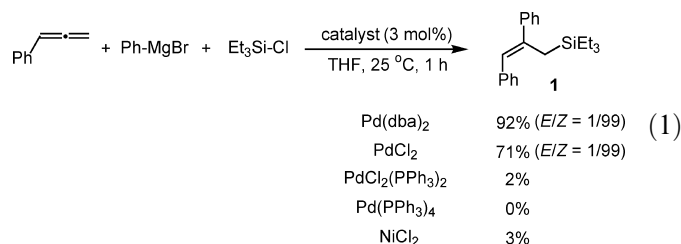
Transition metal-catalyzed reactions which introduce carbon and/or silyl functionalities to C–C unsaturated compounds have been widely used for organic synthesis as useful methods for construction of organic molecules. One of our current projects is the regioselective silylation [1] and alkylation [2] of alkenes and dienes using chlorosilanes and alkyl halides by the combined use of transition metal catalysts and Grignard reagents. During the course of this study, we have found that Pd catalyzes silylation and alkylation of allenes using chlorosilanes and alkyl halides [3].

2. Results and discussions

2.1. Carbosilylation of arylallenes

A typical example is as follows. To a mixture of phenylallene (1.0 mmol), Et₃SiCl (1.3 mmol), and PhMgBr (1.3 mmol) in THF (1.3 mL) was added Pd(dba)₂

(dba = dibenzylideneacetone) (0.03 mmol) at 25 °C under nitrogen, and the resulting mixture was stirred for 1 h at the same temperature. The NMR analysis of the crude mixture indicated the formation of carbosilylated product **1** bearing phenyl group at the central carbon and triethylsilyl group at the terminal carbon in 92% yield and with higher than 99% regio- and stereoselectivities (Eq. (1)). The product was obtained in pure form in 67% yield by column chromatography with hexane as the eluent. In this reaction, only a trace amount of Et₃SiPh (2%) was formed as a byproduct, probably through the direct reaction of Et₃SiCl with PhMgBr. When PdCl₂ was used instead of Pd(dba)₂, **1** was obtained in 71% yield. Under the same conditions, palladium complexes bearing phosphine ligands such as PdCl₂(PPh₃)₂, Pd(PPh₃)₄ and NiCl₂ were ineffective.



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Some other representative results are shown in Table 1. This reaction also proceeded efficiently when Me₃SiCl and Ph₂MeSiCl were used (entries 1 and 2). Chloro and methoxy substituents on the aryl ring remained intact in this reaction system (entries 3 and 4). The use of vinyl and methyl Grignard reagents also afforded the corre-

sponding coupling products **6** and **7** in 72% and 51% yield, respectively (entries 5 and 6) although the stereoisomers were obtained. α -Methyl and phenyl substituted phenylallenes also underwent present coupling reaction (entries 7 and 8). The reaction was sluggish with respect to alkylallenes.

Table 1
Pd-catalyzed carbosilylation of allenes with Grignard reagents and chlorosilanes^a

Entry	Allene	R'-MgBr	R'' ₃ Si-Cl	Product	Yield (%) ^d	E/Z ^e
1		Ph-MgBr	Me ₃ Si-Cl		89	2/98
2			Ph ₂ MeSi-Cl		82 (68)	2/98
3		<i>p</i> -Cl-C ₆ H ₄ -MgBr	Et ₃ Si-Cl		90 (80)	1/99
4		<i>p</i> -OMe-C ₆ H ₄ -MgBr	Et ₃ Si-Cl		87 (75)	1/99
5 ^b			ⁿ Pr ₃ Si-Cl		(72)	30/70
6 ^b		Me-MgBr	ⁿ Pr ₃ Si-Cl		53 (51)	84/16
7 ^c		Ph-MgBr	Et ₃ Si-Cl		84 (72)	93/7
8		Ph-MgBr	Et ₃ Si-Cl		50 (38)	

^a The reaction was carried out unless otherwise stated in THF at 25 °C for 1 h using arylallene (1.0 mmol), Grignard reagent (1.3 mmol), chlorosilane (1.3 mmol), chlorosilane (1.3 mmol), and Pd(dba)₂ (0.03 mmol).

^b Grignard reagent and chlorosilane were used in 1.5 mmol.

^c The reaction was carried out for 9 h.

^d NMR yield. Isolated yield is in parentheses.

^e Determined by GC.

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