Pergamon

Tetrahedron Letters 41 (2000) 8445–8449

TETRAHEDRON
LETTERS

Tetraalkylammonium salt-based catalyst systems for directing Heck-type reactions. Arylation of allyltrimethylsilane

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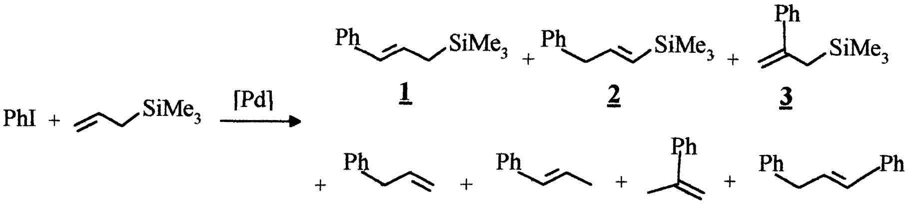
Received 20 July 2000; accepted 6 September 2000

Abstract

An appropriate selection of the [Pd/base/QX] catalyst systems allows one to *direct at will* the palladium-catalysed arylation of allyltrimethylsilane towards the formation of either (*E*)-1-aryl-3-(trimethylsilyl)-1-propene or 3-aryl-1-propene, by preventing or promoting efficiently the desilylation and the double bond migration. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: ammonium salts; arylation; Heck reactions; palladium and compounds.

Palladium-catalysed arylation of allyltrimethylsilane has been the subject of several studies. To achieve this type of reaction with a high selectivity, several problems have to be overcome. The regioselectivity of both the insertion and β-hydride-elimination steps has to be controlled as well as the double bond migration and the chemoselectivity of the reaction which depends upon the relative rates of β-hydride and β-trimethylsilyl eliminations. Formation of a mixture of silylated (1+2+3) and desilylated products (4+6) has been observed in the reaction of iodoben-



Scheme 1.

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PII: S0040-4039(00)01498-2

zene with allyltrimethylsilane (Scheme 1) under traditional Heck conditions, with **1** being the major product.[1] Addition of silver nitrate has been shown not only to suppress the desilylation but also to affect the regiochemistry of both the insertion and subsequent β-hydride-elimination steps as products **2** and **3** were then obtained predominantly (**1**/**2**/**3** = 3/70/27).[1]

Highly regioselective internal arylation of allyltrimethylsilane has recently been realised using aryl triflates as the arylating agent together with 1,1′-bis(diphenylphosphino)ferrocene (DPPF) as the ligand for the palladium catalyst.[2] Intramolecular arylation of allylsilanes with highly selective construction of tertiary sp^3 carbon centres has also been described in the presence of tetraalkylammonium or silver salts.[3,4] Use of silver salts led to highly selective formation of silylated cyclised products,[3] although this effect is cancelled by addition of the ligand (*S*)-BINAP resulting in highly regio and enantioselective formation of tertiary sp^3 carbon centres which occurred with desilylation.[3,4]

We have recently shown[5,6] that a suitable selection of quaternary ammonium salt-based catalyst systems not only enhance the rate and selectivity of Heck-type reactions, but also allows the choice of outcome of the reactions involving 2,3-dihydrofuran[5] or vinyltrimethylsilane.[6] In this paper, we wish to report that tetraalkylammonium salt-based catalyst systems can also be highly effective for Heck-type reactions involving allyltrimethylsilane, not only for achieving them with a high selectivity, under mild conditions, but also for directing them at will towards the formation of either silylated or non-silylated products.

Conditions were first determined for the reaction of iodobenzene with allyltrimethylsilane (Scheme 1 and Table 1). Highly selective formation of (*E*)-1-phenyl-3-(trimethylsilyl)-1-propene **1** was smoothly achieved upon treatment in acetonitrile, *at room temperature*, of iodobenzene with allyltrimethylsilane, in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO), tetra-*n*-butylammonium bromide and catalytic amounts of bis(dibenzylideneacetone) palladium (Table 1, entry 1).

Arylation at the terminal position occurred exclusively as no formation of 2-phenyl-3-(trimethylsilyl)-1-propene **3** was observed. The isomeric (*E*)-3-phenyl-1-(trimethylsilyl)-1-propene **2** was obtained as a minor product (**1**/**2** = 89/11). Allylbenzene **4** was not detected as the desilylated product, but its isomer **5** was observed, although only as a secondary product. Acetonitrile appears more effective than tetrahydrofuran, toluene or *N*,*N*-dimethylformamide for obtaining both a high yield and a high selectivity (entry 1 compared with entries 2, 3 and 4). Tetra-*n*-butylammonium chloride (entry 5) was slightly more efficient than tetra-*n*-butylammonium bromide (entry 1) giving slightly better results. Lower conversion and lower selectivity were both observed in the absence of tetraalkylammonium salt (entry 6) leading, moreover, to a mixture of three isomeric silylated products (**1**/**2**/**3** = 79/13/8). Use of DABCO as base seemed essential for obtaining a high yield of silylated products as desilylation occurred much more readily in the presence of other bases such as triethylamine or diisopropylethylamine (entries 7 and 8). Complex mixtures of silylated and desilylated products were then obtained, the latter being constituted by allylbenzene **4**, 1-phenyl-1-propene **5** and (*E*)-1,3-diphenyl-1-propene **7**. Formation of **7** most probably results from palladium-catalysed arylation of allylbenzene **4** formed in situ; this reaction being in competition with the isomerisation of **4** into **5**, even when reactions were performed with an excess (1.75 equiv.) of allyltrimethylsilane.

Conditions for achieving highly selective desilylation have also been found (entries 9–11). Allylbenzene **4** was obtained without formation of silylated products when the reaction is effected in the presence of tetra-*n*-butylammonium acetate. It is noteworthy that allylbenzene **4** was exclusively obtained; no isomeric products **5** and/or **6** were detected. The described reaction

Table 1

Palladium-catalysed phenylation of allyltrimethylsilane[a,b]

Entry	Base	QX	Solvent	T (°C/h)	Conversion (%)[c]	Silylated products yield (%)[c]	Ratio[d] **1**/**2**/**3**	Yield (%)[c] **4**	**5**	**7**
1[a]	DABCO	n-Bu$_4$NBr	CH$_3$CN	rt/21	100	82	89/11/0	0	14	0
2[a]	DABCO	n-Bu$_4$NBr	THF	rt/26	74	54	80/20/0	0	Traces	0
3[a]	DABCO	n-Bu$_4$NBr	toluene	rt/21	87	82	63/29/8	0	Traces	0
4[a]	DABCO	n-Bu$_4$NBr	DMF	rt/21	90	76	85/15/0	0	12	0
5[a]	**DABCO**	**n-Bu$_4$NCl**[e]	**CH$_3$CN**	**rt/19**	**100**	**87**	**90/10/0**	**0**	**12**	**0**
6[a]	DABCO	None	CH$_3$CN	rt/24	75	61	79/13/8	0	10	0
7[a]	NEt$_3$	n-Bu$_4$NCl[e]	CH$_3$CN	rt/24	82	28	–	12	9	11[f]
8[a]	EtN(i-Pr)$_2$	n-Bu$_4$NCl[e]	CH$_3$CN	rt/21	100	9	–	13	10	28[f]
9[b]	**n-Bu$_4$NOAc**	**n-Bu$_4$NOAc**	**DMF**	**50/24**	**100**	**0**	**–**	**95**[g]	**0**	**0**
10[b]	KOAc	n-Bu$_4$NOAc	DMF	50/24	51	0	–	40[g]	0	0
11[b]	n-Bu$_4$NOAc	n-Bu$_4$NOAc	DMF	rt/48[h]	100	0	–	83[g]	0	0

[a] All reactions were carried out with PhI (1 equiv.), allyltrimethylsilane (1.75 equiv.), Pd(dba)$_2$ (0.03 equiv.), base (2.5 equiv.), and tetraalkylammonium salt (1 equiv.).

[b] Unless otherwise stated, all reactions were carried out with PhI (1 equiv.), allyltrimethylsilane (5 equiv.), Pd(dba)$_2$ (0.03 equiv.), PPh$_3$ (0.09 equiv.), base (1.5 equiv.), and tetraalkylammonium salt (1 equiv.) in the presence of crushed 4 Å molecular sieves.

[c] Determined by GLC analysis against an internal standard (dodecane or hexadecane).

[d] Determined by GC/MS analysis.

[e] Tetrabutylammonium chloride, tech., 95% from Acros.

[f] Based on PhI.

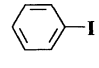
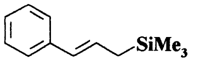
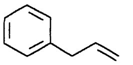
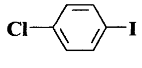
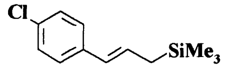
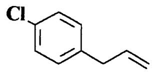
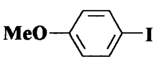
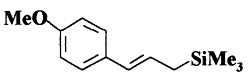
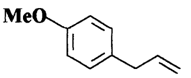
[g] Biphenyl as the only by-product.

[h] In the presence of 0.04 equiv. of Pd(dba)$_2$ and without PPh$_3$.

has thus been realised with a very high regioselectivity in the insertion step and the desilylation achieved without migration of the double bond. Use of tetra-*n*-butylammonium acetate both as base and tetraalkylammonium salt (entry 9) is the most efficient, while a combination of potassium acetate and tetra-*n*-butylammonium acetate is much less effective (entry 10). Formation of allylbenzene 4 can even be achieved under mild conditions, i.e. at room temperature (entry 11). Biphenyl was the only by-product observed in these reactions; its formation can be minimised by effecting reactions in a strictly inert atmosphere.

Optimum conditions have thus been determined to *induce at will* the arylation of allyltrimethylsilane towards the formation of either (*E*)-1-aryl-3-(trimethylsilyl)-1-propene or 3-aryl-1-propene (Table 2 and Scheme 2).

Table 2
Palladium-catalysed arylation of allyltrimethylsilane

ArI	Conditions [a], [b]	Product	Temperature / Time	Yield (%) [c], [d]	Isomeric purity (%) [e]
	I		r.t. / 24h	75 (87)	93 90
"	II		50°C / 24h	80 (95)	100
	I		r.t. / 5 days	70 (80)	94 90
"	II		60°C / 22h	70 (87)	100
	I		r.t. / 20h	60 (74)	97 92
"	II		60°C / 22h	78 (94)	100

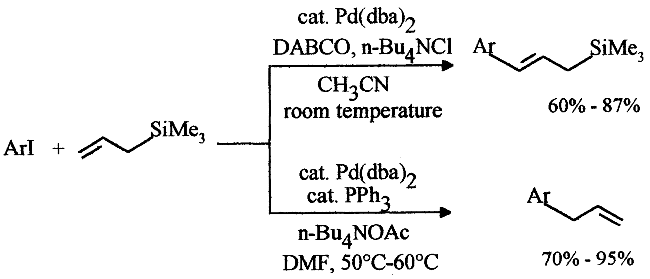
[a] General Procedure (Conditions I): Under an inert atmosphere, to a well-stirrred suspension of DABCO (2.5 - 3 equiv.), n-Bu$_4$NCl (1 equiv.), and Pd(dba)$_2$ (0.03 - 0.04 equiv.) in dry acetonitrile, were successively added the aryl iodide (1 equiv.), and allyltrimethylsilane (1.5 - 2 equiv.). The reaction mixture was then stirred at room temperature for the time indicated. Diethyl ether was then added and the mixture filtered over celite. The filtrate was washed (water and brine), dried (MgSO$_4$), the volatiles evaporated under reduced pressure and the crude product was purified by flash chromatography.

[b] General Procedure (Conditions II): Under an inert atmosphere, a suspension of n-Bu$_4$NOAc (2.5 equiv.) and 4Å molecular sieves (powder or crushed) in dry DMF was stirred at room temperature for 1h - 3h. Pd(dba)$_2$ (0.03 - 0.04 equiv.) and PPh$_3$ (P/Pd # 3-4) were then added, followed by aryl iodide (1 equiv.) and allyltrimethylsilane (5 equiv.). The reaction mixture was then stirred at the temperature and for the time indicated. After cooling to room temperature, diethyl ether was added and the mixture filtered over celite. The filtrate was washed (water and brine), dried (MgSO$_4$), the solvent evaporated and the crude product was purified by distillation or flash chromatography.

[c] Unoptimised yields of isolated products.

[d] Yields in parentheses are determined by GLC analysis against an internal standard (dodecane or tridecane).

[e] Determined by GC/MS analysis.



Scheme 2.

The high regioselectivity observed in the described reactions (Scheme 2) is most probably due to the mild reaction conditions made possible by the use of tetraalkylammonium salts. Although an in-depth understanding of the exact role of tetra-*n*-butylammonium acetate and DABCO is not yet available, the opposing nature of these bases might explain the high and complementary chemoselectivities of the described reactions. An affinity of acetate ion for trimethylsilyl group could account for the preferential desilylation while both the sterically hindered nucleophilicity and the strong basicity of DABCO should favour the competitive β-hydride elimination which leads to the formation of silylated products.

In conclusion, tetraalkylammonium salt-based catalyst systems can be highly useful for Heck-type reactions involving allyltrimethylsilane as not only do they allow one to achieve these reactions under mild conditions, with high regio- and chemoselectivity, but they also allow one to *direct them at will* towards the formation of either silylated or non-silylated products.

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