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LETTERS

Tetraalkylammonium salt-based catalyst systems for directing the arylation of vinyltrimethylsilane

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Abstract:
A suitable choice of [Pd/MZ/QX] catalyst systems can allow to *direct at will* the arylation of vinyltrimethylsilane towards the formation of either (E)-trimethyl (2-arylethenyl) silanes or styrene derivatives.

Keywords: Ammonium salts, Arylation, Heck reactions, Palladium and compounds.

Tetraalkylammonium salts as additives are known to enhance the rate and selectivity of Heck-type reactions. [1-20]. We have recently described the first results showing that these reactions can, moreover, be directed at will by a suitable choice of the [Pd/Base/QX] catalyst system which can either prevent or favour efficiently the migration of the double bond formed [21]. We now wish to report that an appropriate selection of tetraalkylammonium salt-based catalyst systems can also be effective in either suppressing or promoting desilylation.

Palladium-catalysed reaction of aryl halides with vinyltrimethylsilane under standard Heck conditions (5% $Pd(OAc)_2$, 10% PPh_3, NEt_3, DMF, 125 °C) have been described leading selectively to styrene derivatives [22]. Reactions have also been realised without desilylation, under milder conditions (50°C-100 °C) when silver nitrate was added [23, 24]. The results reported herein illustrate the utility of tetraalkylammonium salts in this type of reactions permitting not only to perform them under mild conditions and with high selectivity, but also to achieve them with the desired selectivity.

Appropriate [Pd/MZ/QX] catalyst systems, constituted by a palladium catalyst in combination with an alkali metal or tetraalkylammonium salt (MZ) and a quaternary ammonium salt (QX), were first selected for phenylation of vinyltrimethylsilane (Scheme 1) considered as model reaction. As shown in Table 1, treatment of iodobenzene with vinyltrimethylsilane in N,N-dimethylformamide at room temperature, in the presence of potassium acetate and tetra-n-butylammonium bromide or chloride and catalytic amount of palladium acetate, led to a mixture of (E)-trimethyl(2-phenylethenyl)silane 1 and styrene 2 (entries 1 and 2). A combination of tetra-n-butylammonium acetate with potassium acetate was more efficient for the selective formation of 1, but a relatively low yield was observed (entry 3). Use of tetra-n-butylammonium acetate as both base and quaternary ammonium salt meets all requirements as high selectivity and excellent yield were obtained for the formation of silane 1 (entry 4).

On the other hand, mixtures of products 1 and 2 resulted from the reaction of iodobenzene with vinyltrimethylsilane (entries 5-7) in the presence of hydrated tetra-n-butylammonium (or potassium) fluoride used in conjunction with tetra-n-butylammonium chloride (hydrated or not).

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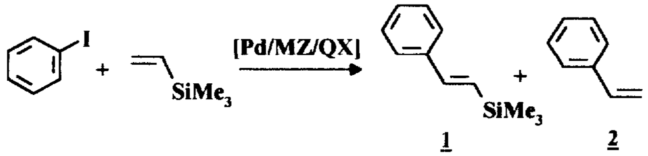
Table 1
Palladium-catalysed phenylation of vinyltrimethylsilane.

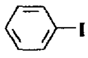
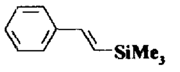
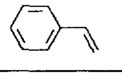
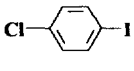
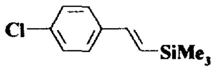
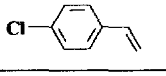
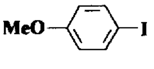
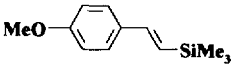
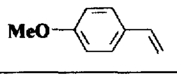
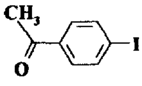
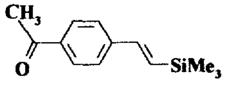
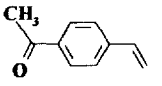
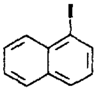
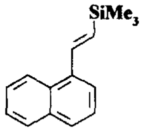
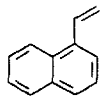


(Scheme 1)

Entry	MZ	QX	Conversion (%) [a]	1 Yield (%) [b]	2 Yield (%) [a]
1	KOAc [c] (2.5 equiv)	nBu$_4$NBr (1 equiv)	53	30.5	18
2	KOAc [c] (2.5 equiv)	nBu$_4$NCl (2.5 equiv)	100	90	10
3	KOAc [c] (2.5 equiv)	nBu$_4$NOAc (1 equiv)	68	68	0
4	**nBu$_4$NOAc** [c], [d] **(1.5 equiv)**	**nBu$_4$NOAc** **(1 equiv)**	**100**	**99**	**traces**
5	nBu$_4$NF, 3H$_2$O [e] (1.5 equiv)	nBu$_4$NCl, xH$_2$O (2 equiv)	97.5	26.5	47.5
6	KF, 2H$_2$O [e], [f] (3 equiv)	nBu$_4$NCl, xH$_2$O (2 equiv)	89	48	41
7	KF, 2H$_2$O [e] (3 equiv)	nBu$_4$NCl (1 equiv)	95	20	68
8	nBu$_4$NF [e], [g] (1.3 equiv)	nBu$_4$NCl (1 equiv)	100	12	83.5
9	**KF** [e] **(3 equiv)**	**nBu$_4$NCl** [h] **(2 equiv)**	**100**	6	**94**

a) Determined by GLC against decane as internal standard.
b) Determined by GLC against tridecane as internal standard.
c) Conditions I: Pd(OAc)$_2$ as catalyst, DMF as solvent, 4Å molecular sieves, room temperature for 24h (reaction times are not optimized) unless otherwise stated.
d) Reaction in DMF or CH$_3$CN.
e) Conditions II: Pd(dba)$_2$ as catalyst, toluene as solvent, room temperature for 24h (reaction times are not optimized) unless otherwise noted.
f) Toluene/water two-phase reaction.
g) Commercially available 1M solution in tetrahydrofuran.
h) In the presence of 4Å molecular sieves.

Table 2:
Palladium-catalysed arylation of vinyltrimethylsilane.

ArI	Conditions [a), b)]	Product	Yield (%) [c), d)]
	I		90 (99)
"	II		86 (94)
	I		92
"	II		79
	I		85
"	II		78
	I		91
"	II		78
	I		94
"	II		86

[a)] General Procedure (Conditions I): To a well-stirred suspension of n-Bu_4NOAc (2 equiv.) and 4Å molecular sieves in dry N,N-dimethylformamide or acetonitrile were successively added the aryl iodide (1 equiv.), vinyltrimethylsilane (1.2 equiv.) and palladium acetate (0.03-0.05 equiv.). The reaction mixture was then conveniently stirred overnight at room temperature (reaction times were not optimized). Diethyl ether was then added and the mixture filtered over celite. The filtrate was washed with water, dried ($MgSO_4$), the solvent evaporated under reduced pressure and the crude product purified by flash chromatography.

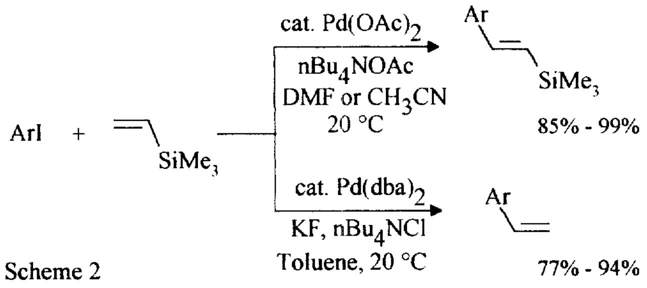
[b)] General Procedure (Conditions II): To a well-stirred suspension of anhydrous potassium fluoride (2-3 equiv.), nBu_4NCl (2 equiv.) and 4Å molecular sieves in dry toluene were successively added the aryl iodide (1 equiv.), vinyltrimethylsilane (3-4 equiv.), and bis(dibenzylideneacetone)palladium (0.03-0.05 equiv.). For convenience, the reaction mixture was then stirred overnight at room temperature (reaction times were not optimized). Work-up was performed as detailed in conditions I.

[c)] Non optimised yields of isolated products.

[d)] Yields in parentheses are determined by GLC against an internal standard.

In contrast, under anhydrous conditions, selective formation of styrene can be achieved (Table 1, entries 8 and 9). In particular, a combination of anhydrous potassium fluoride and tetra-n-butylammonium chloride is most suitable as styrene **2** can then be obtained with high selectivity and in good yield.

Optimum conditions *using tetraalkylammonium salts* (Table 1, entries 4 and 9) have thus been determined to *direct at will* the arylation of vinyltrimethylsilane towards the formation of either (E)-trimethyl (2-arylethenyl)silanes or styrene derivatives (Scheme 2 and Table 2).



Scheme 2

In conclusion, an appropriate selection of tetraalkylammonium salt-based catalyst systems can allow *to prevent or promote at will* the desilylation in arylation of vinyltrimethylsilane, which very probably proceeds via the sequence β-hydride elimination followed by reverse readdition of palladium hydride complex and subsequent desilylation [24]. From the synthetic point of view, these results provide two particularly convenient, selective and efficient catalytic procedures for grafting either a vinylsilane or a vinyl functional group onto an aromatic nucleus, using readily available substrates under mild reaction conditions.

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