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PALLADIUM-CATALYSED ARYLATION OF VINYLTRIMETHYLSILANE IN THE PRESENCE OF SILVER NITRATE

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Abstract: *A series of arylated vinyltrimethylsilanes have been prepared by means of Heck Arylation in the presence of silver nitrate, which serves to suppress the elimination of the silicon group and enhance the reaction rate.*

The importance of vinylsilanes as versatile precursors and their wide applications in organic synthesis are based on the characteristic properties of silicon which allow for example regio- and stereoselective substitutions to occur.[1] Transition metal mediated C-C coupling reactions involving cleavage of the C-Si bond have also found their use, e.g. coupled products are formed via ArCH=CHPd-intermediates after treatment of $ArCH{=}CHSiMe_3$ or $ArCH{=}CHSiF_5^{2-}$ with palladium salts.[2,3] Similarly π-allylpalladium-complexes are obtained by coupling of vinylsilanes after cleavage of the C-Si bond.[4]

We recently reported that treatment of aryliodides with vinyltrimethylsilane in the presence of a palladium catalyst under ordinary Heck Arylation conditions[5] resulted in the formation of styrene derivatives (eq. 1).[6,7]

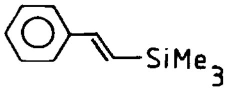
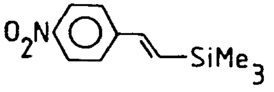
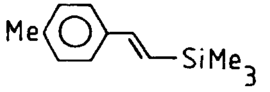
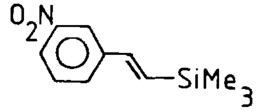
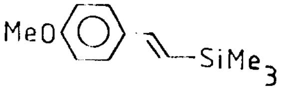
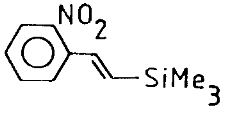
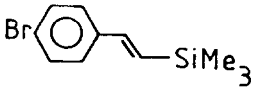
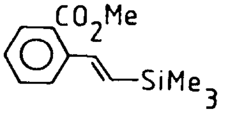
We have now found that the addition of silver nitrate has a strong effect on the outcome of this reaction: The desilylation is completely suppressed and the reaction rate is enhanced considerably (eq. 2).

$$ArI + CH_2{=}CHSiMe_3 \xrightarrow[TEA]{Pd(OAc)_2,PPh_3} ArCH{=}CH_2 \qquad \text{eq. 1}$$

$$ArI + CH_2{=}CHSiMe_3 + AgNO_3 \xrightarrow[TEA]{Pd(OAc)_2,PPh_3} ArCH{=}CHSiMe_3 \qquad \text{eq. 2}$$

The (E)-trimethyl(2-arylethenyl)silanes were isolated in good yields in most cases and according to GC/MS only minor amounts (less than 5%) of isomers were present in the reaction mixture. This reaction seems to be a useful complement to the existing methods for preparation of this type of compounds and merits special attention due to its ease and simplicity. A detailed study of the scope and limitations of this reaction is in progress.

Table: Products after palladium-catalysed arylation of vinyltrimethylsilane with various aryliodides in the presence of silver nitrate[a]

Product	time hr	temp °C	isolated yield[b]	Product	time hr	temp °C	isolated yield[b]
	5	50	32% (GC 95%)		5	50	70%
	5	50	67%		19	50	68%
	5	50	68%		19	100	70%[c]
	16	50	84%		19	80	85%

a) Spectral data were in agreement with the proposed structures b) not optimized
c) around 5% of the aryliodide remained

Typical procedure: Each of the reactants were dissolved or dispersed in acetonitrile (totally 150 ml) and were added to a round-bottomed flask in the following order: Pd(OAc)$_2$ (0.3 mmol), PPh$_3$ (0.6 mmol), AgNO$_3$ (10 mmol), aryliodide (10 mmol), triethylamine (12 mmol), and vinyltrimethylsilane (20 mmol). The flask was then closed and the contents were magnetically stirred and heated for the appropriate time. When the arylhalide has been consumed, the mixture was allowed to cool and then poured into water. After ethereal work-up the crude product was chromatographed on silica (ether/hexane).

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