

# The Effect of Triethylamine on the Palladium-Catalyzed Arylation of Vinyltrimethylsilane

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Nilsson, K. and Hallberg, A., 1990. The Effect of Triethylamine on the Palladium-Catalyzed Arylation of Vinyltrimethylsilane. – Acta Chem. Scand. 44: 288–290.

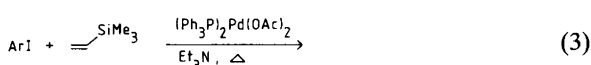
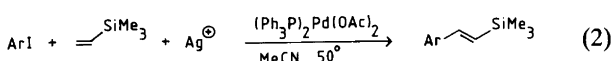
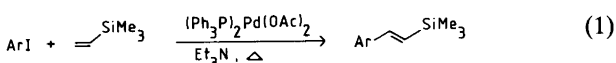
In 1989, Garst and McBride<sup>1</sup> reported that treatment of an aryl iodide with vinyltrimethylsilane, a catalytic amount of palladium(II) acetate and triphenylphosphine in refluxing triethylamine produces arylvinylsilanes [eqn. (1)]. This procedure for aryl substitution was suggested to offer 'advantages over the recently published ones. The aryl halide can be hindered and still yield the desired product and the process 'does not require ... silver.' We have reported a related palladium-catalyzed procedure for the regioselective arylation of vinyltrimethylsilane, in which we used silver ion as a *halide abstractor* in order to suppress the otherwise concomitant desilylation [eqn. (2)].<sup>2,3</sup> The simplified method by Garst and McBride, based on the use of refluxing triethylamine as the solvent,<sup>1</sup> would, if generally applicable, be superior to the Pd(OAc)<sub>2</sub>/Ag<sup>+</sup> procedure.<sup>2</sup>




To evaluate the synthetic potential of the former method we have now performed reactions in triethylamine with four aryl iodides [eqn. (3), (4)]. Iodobenzene (1), 1-iodo-4-

methoxybenzene (2) and 1-iodo-4-nitrobenzene (3) were consumed at 110°C, and furnished mixtures of compounds [eqn. (3)]. The yields of 2-arylethenylsilanes were moderate (50, 29 and 17%, respectively by GLC), partial desilylation occurred and significant amounts of the regioisomers derived from arylation at the internal carbon were obtained (11, 8 and 8%),<sup>4</sup> compared with < 5% in the Pd(OAc)<sub>2</sub>/Ag<sup>+</sup> system.<sup>2</sup> The formation of styrene or stilbene was not observed in the latter reaction medium. The conversion of 1 was much faster in the presence of silver ion; all the iodobenzene was consumed after 5 h at 50°C,<sup>2</sup> while 95% of 1 remained unchanged with triethylamine as the solvent at this temperature. Fair isolated yields of the 2-arylethenylsilanes were obtained by the Pd(OAc)<sub>2</sub>/Ag<sup>+</sup> procedure: 74, 68 and 70%, respectively.<sup>2</sup>

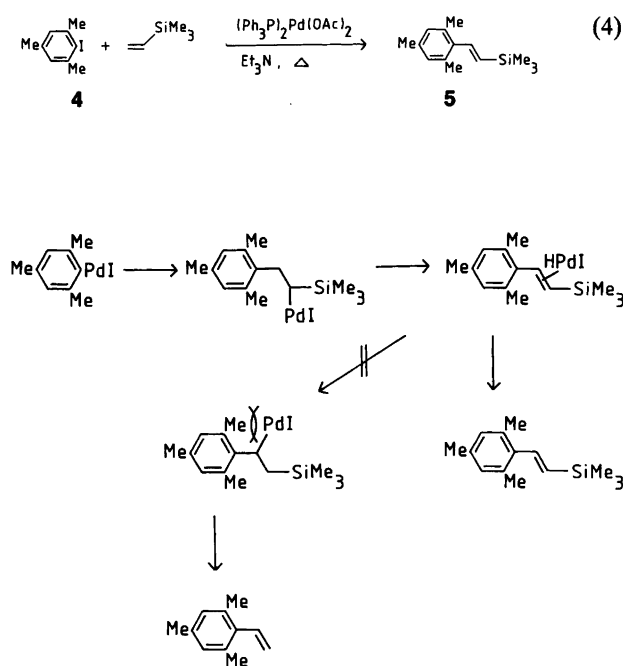
Under ordinary Heck reaction conditions<sup>5</sup> (a slight excess of amine in the absence of silver ion), 1 gave 28% of 2-phenylethenylsilane, 10% of 1-phenylethenylsilane, 38% of styrene and 9% of stilbene, in toluene after 5 days at 90°C.<sup>6</sup> We presume that the lesser extent of desilylation found in triethylamine results from an amine-promoted elimination of HPdI from the π-system, before readdition and subsequent halide-induced cleavage of the silicon-carbon bond.<sup>7</sup> However, the results reported by Garst and McBride on the preparation of hindered 2-arylethenylsilanes,<sup>1</sup> were more likely the result of steric interaction with *ortho* substituents that hinders the readdition of HPdI, than an effect of the amine *per se*. We have subjected 1-iodo-2,4,6-trimethylbenzene (4) to the reaction conditions in triethylamine at 110°C and isolated (*E*)-trimethyl[2-(2,4,6-trimethylphenyl)ethenyl]silane (5) in 67% yield [93% GLC, eqn. (4)]. Furthermore, a good yield of 5 (79% GLC) was also obtained after reaction of compound 4 in *toluene*, at the same reaction temperature, showing the importance of steric interactions for the suppression of desilylation (Scheme 1). More of the corresponding styrene was observed in toluene (17%) than in triethylamine (3%), reflecting the tendency of the amine, acting as a ligand/base,<sup>8</sup> to suppress desilylation.

Several good procedures have been reported for the preparation of (*E*)-trimethyl(2-arylethenyl)silanes.<sup>2,9</sup> The Pd(OAc)<sub>2</sub>/Ag<sup>+</sup> method is preferable in most cases when aryl iodides are available as starting materials [eqn. (2)].<sup>10</sup>



	Ar-CH=CHSiMe <sub>3</sub>	Ar-C(CH <sub>3</sub> )=CHSiMe <sub>3</sub>	Ar-CH=CH <sub>2</sub>	Ar-CH=CH-Ar	unidentified products and biaryls
 1	50	11	22	13	4
 2	29	8	22	27	14
 3 (+ 7% Z-isomer)	17	8	1	–	67

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Scheme 1.

The present study supports the work of Garst and McBride [eqn. (1)]<sup>1</sup> as a means of preparing *sterically hindered* derivatives but shows it to be of little synthetic value for simple systems.

### Experimental

**Materials.** Palladium(II) acetate, vinyltrimethylsilane, iodobenzene, 1-iodo-4-nitrobenzene, 1-iodo-4-methoxybenzene and 1-iodo-2,4,6-trimethylbenzene were used as received from commercial sources. Triphenylphosphine was recrystallized from ethanol, triethylamine was distilled from CaH<sub>2</sub>, and toluene was distilled and stored over appropriate molecular sieves.

**General.** <sup>1</sup>H NMR spectra were recorded on a Varian XL300 spectrometer with Me<sub>4</sub>Si as an internal standard. Mass spectra were recorded on a Finnigan 4021 (Data System Incos 2100) mass spectrometer at an ionizing voltage of 70 eV. Flash chromatography was performed as described by Taber,<sup>11</sup> using 70 g TLC-silica gel 60 H (15 μm, Merck, No. 11695) and a Ø50-mm column. GLC analyses were carried out on a Varian 3300 instrument equipped with a 2 m glass column of 5% OV17 on Chromosorb W. GLC yields were determined by a standard addition procedure. Elemental analyses were performed by The Micro-analytical Laboratory at the University of Lund, Sweden. All the reactions were carried out in a 50 ml, thick-walled and thin-necked Pyrex tube.

**General procedure for the arylation of vinyltrimethylsilane in triethylamine.** Palladium(II) acetate (27 mg, 0.12 mmol)

was added to a stirred solution of vinyltrimethylsilane (1.20 g, 12 mmol), triphenylphosphine (58 mg, 0.22 mmol), aryl iodide **1**, **2** or **3** (5.5 mmol) in 12.5 ml of deaerated triethylamine. The reaction tube was flushed with argon, sealed with a screw-cap and heated at an inner temperature of 110 or 90°C for 72 h. Compound **2** required a reaction time of 72 h at 110°C for full conversion. The mixture was partitioned between diethyl ether and water, and the organic phase was analyzed by GLC [for results at 110°C, see eqn. (3)]. A similar product distribution was obtained from **1** at 90°C. Monitoring of the reaction of **1** showed that the arylethenylsilane/styrene (stilbene) ratio was independent of reaction time. Reaction of **1** in a round-bottomed flask equipped with two condensers, at reflux and under argon (inlet and outlet through a septum at the top of the upper condenser), gave a similar ratio of silylated/desilylated products as in the sealed systems. (A large amount of stilbene was obtained, suggesting that vinyltrimethylsilane had escaped.)

*In toluene.* The reactions in deaerated toluene (12.5 ml) at 90 or 110°C were performed in a sealed tube in the same manner as described above, except for the addition of only 1.2 equiv. of triethylamine (668 mg, 6.6 mmol).

(*E*)-Trimethyl[2-(2,4,6-trimethylphenyl)ethenyl]silane (**5**). Palladium(II) acetate (27 mg, 0.12 mmol) was added to a stirred solution of vinyltrimethylsilane (1.20 g, 12 mmol), triphenylphosphine (58 mg, 0.22 mmol), 1-iodo-2,4,6-trimethylbenzene (1.35 g, 5.5 mmol) in 12.5 ml of deaerated triethylamine. The reaction vessel was flushed with argon, sealed and heated at 110°C for 72 h. The reaction mixture was allowed to cool and was thereafter diluted with diethyl ether (25 ml), filtered and poured into 50 ml of water. After extraction with diethyl ether (4×25 ml), the combined organic phases were washed with 25 ml of water, dried (MgSO<sub>4</sub>), and evaporated. The crude product was subjected to flash chromatography using pentane as the eluent (30 ml fractions were collected) to give 0.80 g (67%) of a colourless oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.17 (s, 9 H), 2.20 (s, 3 H), 2.25 (s, 6 H), 5.91 (d, 1 H, *J* 19.7 Hz), 6.86 (d, 1 H, *J* 19.7 Hz), 6.86 (br s, 2 H); MS (*m/z*): 218 (M<sup>+</sup>). Anal. C<sub>14</sub>H<sub>22</sub>Si: C, H.

**Acknowledgements.** We gratefully acknowledge support through grants from the Swedish Natural Science Research Council.

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## SHORT COMMUNICATION

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Received August 23, 1989.