

STYRENE DERIVATIVES VIA PALLADIUM-CATALYZED  
VINYLATION OF ARYL IODIDES

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A new and efficient method for the preparation of styrene derivatives via Pd-catalyzed vinylation of aromatic systems, using vinyltrimethylsilane as an ethylene equivalent, is described.

Styrene derivatives are often very useful chemical intermediates. Frequently, however, the synthesis of such compounds proves not to be trivial. Recently a useful method for the preparation of a wide variety of styrene derivatives via palladium-catalyzed arylation of ethylene, was reported by Heck et al.<sup>1</sup> An ethylene pressure of 100-120 psi was found to give optimum yields. Palladium-catalyzed arylation of vinyl acetate starting from 5-iodopyrimidines gave good yields of 5-vinylpyrimidines,<sup>2</sup> while the same reaction applied to iodobenzene resulted in a mixture of products, the amount of styrene never exceeding 20 %.<sup>3</sup>

In connection with our studies on palladium-catalyzed arylation of vinyl ethers,<sup>4</sup> and the use of organosilicon compounds in organic synthesis,<sup>5</sup> vinyltrimethylsilane was treated with four different aryl iodides in the presence of a palladium catalyst. This turned out to be a convenient method for the preparation of styrene derivatives in 50-60 % yields (see Table I).

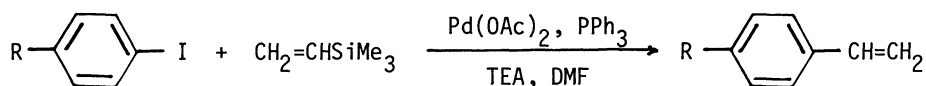


Table I. Pd-catalyzed vinylation of aryl iodides

R	H	MeO	NO <sub>2</sub>	Me
Yield of styrene <sup>a)</sup>	60 % <sup>b)</sup>	60 % <sup>c)</sup>	58 % <sup>d)</sup>	51 % <sup>e)</sup>

a) GLC yields, not optimized; b) 125°C, 0.5 h; c) 70°C, (o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, 48 h; d) 85°C, 12 h; e) 85°C, 24 h.

Using  $\text{Pd}(\text{OAc})_2/\text{PPh}_3$  as catalyst, triethylamine (TEA) as base and DMF as solvent, iodobenzene was completely consumed within 0.5 h at 125°C. Longer reaction times (4 h, 65 h) at lower temperatures (85°C, 55°C) were equally effective. Absence of the phosphine ligand as well as the use of toluene as solvent resulted in considerably lower yields. Pd/C(10%) gave a 30-50% yield of styrene.

In addition to styrene smaller amounts (5-25 %) of E-trimethyl-(2-phenylethylene)silane were formed in all cases. Minor amounts of an isomeric silane were also detected by GLC/MS.

Although no mechanistic studies have been made, it seems reasonable to assume that a palladium-promoted cleavage of the vinyl-silicon bond is involved.<sup>6,7</sup>

Typical experimental procedure: Iodobenzene (0.882 mmol), vinyltrimethylsilane (2.20 mmol), TEA (1.20 mmol),  $\text{PPh}_3$  (0.036 mmol) and  $\text{Pd}(\text{OAc})_2$  (0.018 mmol) were dissolved in 15 ml of DMF. The mixture was degassed ( $\text{N}_2$ ) and then heated at 125°C in a closed flask. The progress of the reaction was monitored by GLC (OV 101, 3 %, 2.5 m). When all of the iodobenzene had been consumed (0.5 h), the mixture was allowed to cool and then poured into water. After ethereal work-up the crude product was analyzed by GLC, using diphenyl methane as internal standard.

In conclusion the method described above using vinyltrimethylsilane as an ethylene equivalent<sup>8,9</sup> seems to be a useful complement to existing methods for vinylation of aryl halides. What especially merits attention is the very simple preparative procedure, with no need for pressure-vessels.<sup>1</sup> A detailed study of the scope and limitations of this reaction is in progress.

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