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Heck-type Reaction of Iodotrimethylsilane with Olefins Affording Alkenyltrimethylsilanes

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Iodotrimethylsilane reacted with styrene derivatives in the presence of triethylamine and a palladium catalyst to give β-styrylsilanes.

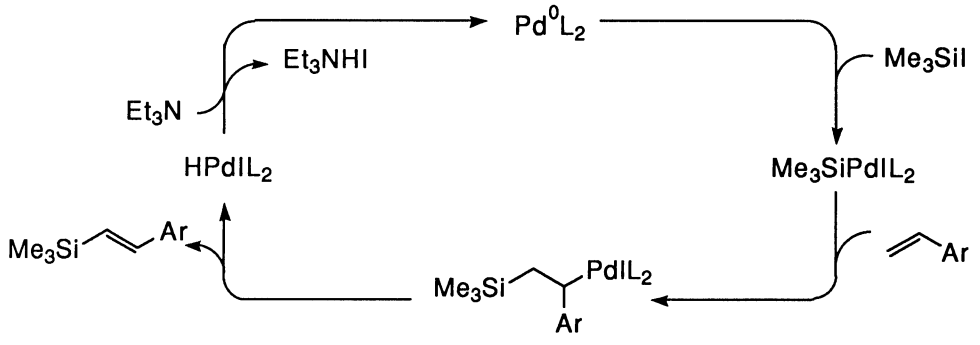
Increasing attention has been directed toward organosilicon compounds because of their synthetic utilities and physicochemical properties.[1)] In this sense, new synthetic methods for silicon chemicals are important for the future of this promising field. As is widely known, organic halides readily undergo oxidative addition to low valent transition metal complexes, and the process has been proved to be a key elemental step involved in a wide range of useful catalytic reactions.[2,3)] On the other hand, oxidative addition of halosilanes has been believed hard to proceed. However, our previous papers have reported that the reaction does take place with platinum(0) or iridium(I) complexes.[4,5)] Further studies along this line have disclosed that iodotrimethylsilane reacts with olefins in the presence of palladium complex catalysts to give alkenylsilanes. Preliminary results of this new catalytic reaction, which provide the first experimental demonstration of the Heck-type reaction of halosilanes, will be reported in this letter.

A mixture of iodotrimethylsilane (0.5 mmol), styrene (2.0 mmol), triethylamine (0.3 cm^3), and dichlorobis(triethylphosphine)palladium (0.05 mmol) was heated in a sealed ampoule at 120 °C for 72 h. GC analysis of the resulting mixture revealed that trans- and cis-β-trimethylsilylstyrene (**1a**) was formed in 54 and 0.3% yield, respectively, Eq. 1. Ether and water were poured into the mixture, and ether layer was separated and dried by anhydrous $MgSO_4$. Concentration of ether layer followed by preparative TLC (hexane-ether, v/v = 5/1) gave pure **1a** (trans/cis = > 99/1, 37 mg, 42%).[6)] Under the same conditions, p-chlorostyrene and p-methylstyrene reacted to give the corresponding silylstyrene derivatives (**1b**, **1c**) in 44 and 45% yield, respectively (trans/cis = > 99/1).[6)] In addition, a similar reaction of p-methylstyrene in the presence of dichlorobis(tributylphosphine)palladium (0.02 mmol) afforded **1c** in 42% yield (trans/cis = > 99/1).

$$RCH{=}CH_2 + Me_3SiI + NEt_3 \xrightarrow{\text{Pd complex}} \underset{\mathbf{1}}{RCH{=}CHSiMe_3} + NEt_3HI \qquad (1)$$

Yield of **1** / % **a**: R = Ph, 54; **b**: R = p-ClC_6H_4, 44; **c**: R = p-MeC_6H_4, 45

Based on the well established mechanism of Heck-type reactions of organic halides with olefins, the present reaction is safely envisaged to proceed via the reaction sequence shown in Scheme 1. Considering the reactivity of halosilanes toward platinum(0) complexes,[4)] the addition toward palladium(0) is also likely to occur. The subsequent step is believed to be the insertion of an olefin into the silyl-metal intermediate,[7)] although such elemental step is still controversial in relation to the hydrosilylation mechanism.[8)] To verify this



Scheme 1.

elemental step involved in the present catalysis, trans-$Me_3SiPtBr(PEt_3)_2$ (0.05 mmol) was allowed to react at 120 °C for 5.5 h with a benzene-d_6 solution of styrene (0.25 mmol) and triethylamine (0.25 mmol) in an NMR tube. Since the starting complex is, in the absence of bromotrimethylsilane, thermally unstable, most of the silyl moiety came off to afford bromotrimethylsilane (> 70%).9) However, we could observe the formation of trans- and cis-**1a** by GC-MS and GC analyses in 1.8 and 0.5% yield, respectively. Considering the similarity in the reactivity between Pd and Pt complexes, the insertion step may proceed more efficiently under the catalytic conditions in the presence of large excess of iodotrimethylsilane.

In summary, the results described herein open up a possibility of new catalytic reactions based on halosilanes.10) Search for more efficient catalysts and extension to other olefins are under way.

We have been informed of similar results being found by Professor Kohei Tamao. We thank him for sharing his results with us prior to publication.

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6) Satisfactory IR, ^{1}H NMR, and MS spectra were obtained for **1a**, **1b**, and **1c**.

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9) Hexamethyldisiloxane seemed to be formed in about 20% yield as judged from the ^{1}H NMR spectrum of the reaction mixture, though the origin of oxygen was ambiguous.

10) We have been informed that Murai et al. is finding a new catalytic reaction which involves insertion of acetylene into the Si-Pd bond. S. Murai and N. Chatani, private communication.

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