METHYLATION AND PHENYLATION OF OLEFINS BY SILANES IN THE PRESENCE OF PALLADIUM COMPOUNDS

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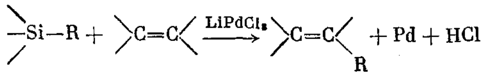
It is known that the methyl and aryl derivatives of mercury, lead, tin, and other metals, alkylate olefins in the presence of palladium compounds [1]. The role of the palladium salt consists in cleavage of the element–carbon bond. The intermediate formation of the organic derivative of palladium occurs here, which either alkylates or arylates the olefin.

Reactions of this type could be accomplished for organosilicon compounds only for the unsaturated derivatives of silicon. Thus, it was shown that allylsilanes are cleaved by palladium salts with the formation of π-allylpalladium chloride [2]. Transfer of the vinyl group to the olefin in the presence of a palladium salt was accomplished for vinylsilanes [3].

It is known that the silicon–methyl bond is cleaved in the presence of some salts of the transition metals.

In the present paper we were able to accomplish the transfer of methyl and phenyl radicals from the silicon atom to the olefin under the influence of lithium palladium chloride. The reaction proceeds by the scheme:



$$\mathrm{\geq Si{-}R} + \mathrm{>C{=}C<} \xrightarrow{\mathrm{LiPdCl_4}} \mathrm{>C{=}C<_{R}} + \mathrm{Pd} + \mathrm{HCl}$$

$R = CH_3, C_6H_5$

Thus, tetramethylsilane reacts with styrene in the presence of a lithium palladium salt in acetonitrile (60°C, 7 h) to give β-methylstyrene in 30% yield; the reaction of tetramethylsilane with cyclohexene (100°, 20 h) gives methylcyclohexene in 86% yield; trimethylphenylsilane reacts with styrene in the presence of a palladium salt in methanol (60°, 7 h) to give stilbene in 50% yield, and ~2% of β-methylstyrene (for all of the experiments the yields were based on the lithium palladium salt).

LITERATURE CITED

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