

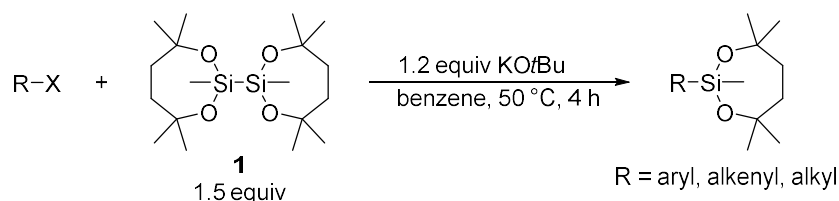
Silylation of Organic Halides with a Disilane Having Seven-Membered Dialkoxysilyl Groups Activated by Potassium *tert*-Butoxide

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Keywords: Silylation; Alkoxysilane; Disilane; Organic Halide

We recently reported the discovery of a dialkoxysilyl group bearing a bulky 7-membered ring that has both excellent stability and on-demand reactivity.¹ This silyl group is stable even during transformations using LiAlH_4 and $n\text{BuLi}$. Still, it is reactive in cross-coupling, Tamao–Fleming oxidation, and bromination under suitable conditions. While seeking for new methods to introduce this useful silyl group, we focused on the silylation of aryl halides using a silylanion species *in situ* generated from a disilane and an alkoxide base.²

We first synthesized tetraalkoxydisilane **1** from commercially available 1,1,2,2-tetrachloro-1,2-dimethyldisilane and 2,5-dimethyl-2,5-hexanediol. Disilane **1** was obtained as a white solid that was found to be stable under air for at least 4 months. Next, we optimized the reaction conditions for silylation of aryl halides with **1**. After optimization, the conditions “1.5 equiv **1**, 1.2 equiv KO^tBu , 4 h, 50 °C in benzene using aryl chlorides as substrates” were found to be optimal. In this silylation reaction, KO^tBu was specifically effective as an activator. We also attempted to introduce silyl groups other than dioxasilepanyl group under the reaction conditions, however, silylation reaction did not proceed at all and an aryl chloride was fully recovered. During the investigation of substrate scope, we found that silylation of alkenyl and alkyl chlorides also takes place. In addition, we conducted some experiments using organic chlorides to disclose the reaction mechanism. Our current mechanistic hypothesis is that chlorine-potassium exchange initially occurs between organic chlorides and *in situ* generated silylpotassium species, followed by the generation of organopotassium species and a chlorosilane.



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