Arenium Carborates Catalyze the Halodealkylation of Tetraalkyl Silanes

Significance: Oestreich, Klare and He report an arenium ion-catalyzed halodealkylation of tetraalkyl silanes. A trimethylsilylium carborate salt activates the halide source, which then engages in a Friedel–Crafts alkylation with benzene, enabling the regeneration of the true catalytic species, an arenium carborate that acts as a strong Brønsted acid for the protodealkylation of quaternary silanes. The reaction is highly selective toward the substitution of smaller alkyl groups and furnishes the resulting halogenated trialkyl silanes in very good to excellent yields.

Comment: Although halosilanes are commonly employed as precursors for the synthesis of silicon-containing compounds, conventional methods for their preparation suffer from poor chemoselectivity and, consequently, purification challenges. In contrast, fully alkylated silanes are inert and thus considered less synthetically valuable. The authors’ report demonstrates that aliphatic silanes can be selectively converted into various heteroleptic halosilanes, which are highly amenable to further manipulations.