Synthesis of Propargyl Silanes from Propargyl Pivalates via C-O Bond Cleavage by Ca-Promoted Reductive Silylation

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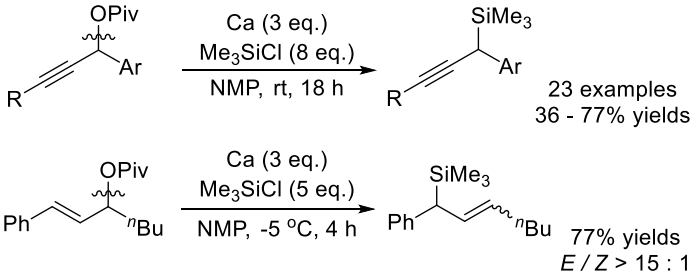
Cross-coupling reactions via C-O bond cleavage have been utilized as a versatile yet powerful method for forming complex organic molecules. Many efforts have been undertaken on silylation via less reactive C-O bond cleavage to date.[1)] However, the development of useful silylation strategies via less reactive C-O bond cleavage, especially silylation of less reported C(sp3)-O electrophiles under catalyst-free conditions, has remained a challenge. We previously reported the reductive silylation of activated vinyl triflates with chlorotrimethylsilane by electron transfer from magnesium.[2)] With our continuous interest in organosilicon chemistry, we herein present our efforts towards propargyl and allyl silanes from the readily accessible propargyl and allyl pivalates via calcium-promoted C(sp3)-O bond cleavage.

Calcium is a vastly abundant, inexpensive, air-stable, and commercially available metal. The use of calcium metal for reductive coupling reactions is unexplored to date. In this study, we commenced our study by choosing propargyl pivalate prepared from 1-hexyne, benzaldehyde, and pivaloyl chloride as the model substrate. As a result, the reductive coupling reaction of propargyl pivalate with chlorotrimethylsilane in the presence of calcium granules gave a propargyl silane in 77% isolated yield. The optimized reaction conditions were fully studied and applied to diverse propargyl pivalates to give a series of propargyl silanes in 36-77% yields. In addition, the reaction of aromatic allyl pivalate also gave the corresponding allyl silane in good yields via allylic arrangement. This reaction provides an efficient approach to synthesize various propargyl and allyl silanes with good yields under mild reaction conditions. Reaction mechanism will be also presented in detail.



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