

Cross-Coupling of Aromatic Bromides with Allylic Silanolate Salts

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The salts of allyldimethylsilanol and 2-butenyldimethylsilanol undergo palladium-catalyzed cross-coupling with a wide variety of aryl bromides to afford allylated and crotylated arenes. The coupling of both silanolates required extensive optimization to deliver the expected products in high yields. The reaction of allyldimethylsilanol takes place at 85 °C in DME with [allylPdCl]₂ (2.5 mol %) to afford 73-95% yields of the allylation products. The 2-butenyldimethylsilanol (*E/Z*, 80:20) required the π -acidic dibenzylideneacetone ligand to achieve high γ -selectivities, and yields of 40-83% were obtained. Configurationally homogeneous (*E*)-silanolates gave slightly higher γ -selectivity than the pure (*Z*)-silanolates. A unified mechanistic picture involving initial γ -transmetalation followed by direct reductive elimination or σ - π isomerization can rationalize all of the observed trends.

