

Development of New Synthetic Reactions Featuring Tandem Carbon-Carbon Bond Formation

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Development of new synthetic reactions that features a tandem process triggered by Brook rearrangement, a C-to-O 1,2-anionic shift of a silyl group, will be discussed.

A basic motif for the strategy is the generation of an α -siloxy carbanion by the reaction of acylsilanes with ketone enolates and then trapping the anions by intra- and inter-molecular electrophiles. For example, the reaction of benzoyltrimethylsilane with lithium enolates of methyl ketones produced 1,2-cyclopropanediols via Brook rearrangement of the initial 1,2-adduct and subsequent internal aldol reaction. This concept was applied to the synthesis of five- and seven-membered carbocycles using the reaction of acryloylsilanes with enolates of alkyl and alkenyl methyl ketone, respectively. Furthermore, we found that the use of enolate of 2-cycloheptenone instead of the enolates of alkenyl methyl ketone as the four-carbon unit in the [3 + 4] annulation produces bicyclo[3.3.2]decenone derivatives, in which the two-atom internal tether could be cleaved to give the *cis*-3,4,8-trisubstituted cyclooctenone enol silyl ethers stereoselectively.

The α -siloxy carbanions can be also generated by an γ -anion-induced ring cleavage of α,β -epoxysilanes. Thus, *O*-silyl cyanohydrins of β -silyl- α,β -epoxyaldehyde can function as a highly functionalized homoenolate equivalent via the tandem sequence involving base-promoted ring opening, Brook rearrangement, and alkylation at the allylic position. Based on these results, we developed several new synthetically useful reactions, in which three methods for the generation of a carbanion at the γ -position, deprotonation, reaction of acylsilanes with a nucleophile followed by Brook rearrangement, and a conjugate addition of a nucleophile to an enoate system bearing an epoxysilane moiety at the α -position, were used.