Stereochemistry of Nucleophilic Substitution Reaction of Halogenosilanes with Silyllithium and Selective Functionalization of Optically Active Disilanes Therefrom

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Optically active disilane derivatives are versatile precursors for polymers with silicon-silicon moiety, such as oligo- and poly(silane)s including dendrimers and (disilanylene-π-conjugated systems)s, to which considerable attention has been paid because of their unique electrical and optical properties. Novel unique properties will be expected based on their stereoregularity different from those without controlled stereoregularity. In this thesis, stereochemistry of substitution reactions of optically active halosilanes with silyllithiums at each chiral silicon atoms was revealed, and regio- and stereoselective functionalization of optically active bifunctionalized disilane derivatives was described.

Stereochemistry crossover from retention to inversion of configuration at about – 20 °C was observed in the nucleophilic substitution of optically active (*R*)-fluoro[methyl(1-naphthyl)phenyl]silane (*R*)-$\mathbf{2_F}$ (> 99% ee) with achiral silyllithium, dimethyl(4-methoxynaphth-1-yl)silyllithium **1** to give optically active 1,1,2-trimethyl-(4-methoxynaphth-1-yl)-1-(1-naphthyl)disilane **3**. Additives, such as HMPA, $LiClO_4$ or LiBr in **1**, have significant effects on the stereoselectivity. It became possible to synthesize both enantiomerically pure stereoisomers of disilane with one chiral center from single antipode of fluorosilane enantiomer.

Stereochemistry of the reaction of methyl(1-naphthyl)phenylhalogenosilnae **2** (in THF) with methyl(1-naphthyl)phenylsilyllithium (in pentane) at – 78 °C is elucidated as inversion for the halogenosilanes, and retention for the silyl anion by XRD. Silicon-(4-methoxynapth-1-yl) bonds of (*R*)-1,1,2-trimethyl-1-(4-methoxynaphth-1-yl)-2-(1-naphtyl)phenylsilane (*R*)-**3** ((*R*); 95% ee) is regioselectively (also stereoselectively for the latter) cleaved on bromination, followed by stereoselective cleavage of the remaining chiral silicon-naphthyl bond (96% inversion) or second silicon-(4-methoxynaphth-1-yl) bond. Cleavage of silicon-silicon bond of the intermediately formed monobromosilane is suppressed by the introduction of the first bromine group.