

Title	シリコン-インターエレメント結合を有する化合物の立体特異的変換と分離
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Stereospecific transformation and separation of silicon-interelement linkage compounds

Their application in the synthesis of stereoregular silicon-containing polymer

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In this work, stereoregular and optically active σ - π conjugated polymers with asymmetric silicon atoms in the main chain was synthesized for the first time by using optically active organosilicon monomers.

Optically active (*S*)-methyl(1-naphthyl)phenylsilyllithium (96 %ee), was prepared by the cleavage of silicon-tin bond of (*S*)-methyl(1-naphthyl)phenylsilyltrimethylstannane with methylolithium. The configuration of the silyllithium is stable for at least 1 hour at -78 °C in tetrahydrofuran. Naphthyl-substituted optically active silyllithium will find wide applicability to obtain a variety of optically active silicon compounds.

The stereochemistry in addition reactions of optically active ethynylsilyl compounds was studied. For optically pure monomer, (+)-1,2-diethynyl-1,2-dimethyl-1,2-diphenyldisilane was separated by preparative chromatography. This is the first example of isolating optically pure disilane with two chiral center. Firstly, dimerization reaction of optically active ethynyl silanes was attempted. The silicon atom of intervening Si(CH₃)Ph unit of obtained homopolymer worked as a “stereochemical probe” to detect and provide information about the configuration of the main chain, and poly[(1, 2-dimethyldiphenyldisilanylene)-butenyne-1, 4-diyl] from optically pure monomer was proved to be highly stereoregular.

In the next, the Heck reaction of optically active ethynylsilyl compounds was studied. For optically pure monomer, (-)-(4-bromophenyl)ethynylmethyl(1-naphthyl)silane and (-)-1,2-diethynyl-1,2-dimethyl-1,2-di(1-naphthyl)disilane were separated by HPLC. The ¹H and ¹³C NMR analysis of the polymer containing disilane units proved the complete retention of asymmetric silicon atoms in the polymerization. The polymer is reasonably considered optically pure (>99%).

The stereochemistry in hydrosilylation reactions of optically active ethynylsilyl compounds was also studied. The product of hydrosilylation polyaddition depends on reaction conditions such as catalyst, temperature. The hydrosilylation reaction in the presence of 5.0 mmol% RhI(PPh₃)₃ at 60°C to give (*E*)-isomer proceeded with retention stereospecificity at the asymmetric silicon center.