Borane-Catalyzed Double Sila-Friedel-Crafts Reaction for the Synthesis of Silacycles

董, 亜芳

氏　　名　：Dong Yafang
Name

論 文 名　：Borane-Catalyzed Double Sila-Friedel–Crafts Reaction for the Synthesis of Silacycles（ホウ素触媒を用いる連続的なシラフリーデルクラフツ反応による含ケイ素環状化合物の合成法の開発）
Title

区　　分　：甲
Category　Kou

論 文 内 容 の 要 旨
Thesis Summary

This dissertation focuses on the investigation of sila-Friedel–Crafts reaction for the synthesis of silacyclic compounds. The direct synthesis of silacycles is challenging because it generally relies upon the lithiation of the corresponding dihalogenated substrates and sequential reaction of the dilithiated intermediates with dichlorosilanes. However, these reactions have some problems, such as the waste of stoichiometric reagents, the tolerance of functional groups, and the difficulty in the synthesis of multi-substituted starting materials. Hence, the efficient and versatile synthetic methods of silacyclic compounds are still desirable.

Recently, kuninobu and other research groups reported iridium- or rhodium-catalyzed intramolecular C–H silylations for the synthesis of silafluorenes, phenazasilines, and silepins. The intra- and intermolecular sila-Friedel–Crafts reaction is appearing as an efficient tool to construct C–Si bonds. Inspired by the intermolecular sila-Friedel–Crafts reaction of aniline derivatives with hydrosilanes, I envisioned that double sila-Friedel–Crafts reactions between biphenyls/biaryl derivatives/terphenyls and dihydrosilanes are ideal and efficient synthetic methods of highly substituted silacyclic compounds.

In Chapter 1, C(sp^2)–H silylation for organosilanes and its applications to the synthesis of π-conjugated molecules is introduced. Here, I briefly survey the progress of research activities regarding transition metal-catalyzed C(sp^2)–H silylation and sila-Friedel–Crafts reactions.

Chapter 2 describes the silafluorene synthesis from amino-substituted biphenyls and dihydrosilanes through a borane-catalyzed double sila-Friedel–Crafts reaction. This reaction system is suitable for the synthesis of multisubstituted silafluorenes, spirosilabifluorenes, and silicon-bridged terphenyl compounds, which are not readily obtained using traditional synthetic methods. Besides, the transformation of the amino groups in those silafluorene derivatives into other substituents was achieved by the cross-coupling reaction between ammonium salts and Grignard reagents.

In Chapter 3, the synthesis of six-membered silacycles, including phenoxasilin and phenothiasilin derivatives is detailed. The borane-catalyzed double sila-Friedel–Crafts reaction of amino group-containing diaryl ethers and dihydrosilanes afforded phenoxasilin derivatives with moderate to excellent yields. Diaryl thioethers was also converted to the corresponding six-membered silacyclic products under the optimal conditions. In addition, the gram-scale synthesis of a selected phenoxasilin and the conversions of amino groups were investigated.

Chapter 4 focuses on the synthesis of seven-membered silacycles, tribenzosilepin derivatives. During the investigation for the synthesis of a silafluorene derivative using a terphenyl substrate, the corresponding tribenzosilepin was obtained in 87% yield. The optimal reaction system was applied to the synthesis of other silepin derivatives with different substituents on the center benzene ring or using other hydrosilane reagents, such as dimethylamino-, difluoro-, naphthalene backbone-containing silepin and 5-silaspiro[4.6]silepin. Besides, a bidirectional reaction forms bissilepin compound. The transformation of the amino groups in tribenzosilepin derivatives to aryl groups and the enlargement of the π-system in tribenzosilepin were realized. The optical properties of some selected tribenzosilepin derivatives were investigated by UV/Vis absorption and photoluminescence spectroscopy.