

炭素三員環とシリル基の特性を利用した立体選択的 合成反応の開発

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2001 Fiscal Year Final Research Report Summary

Stereoselective Synthesis Using iVee-Membered Carbon Ring and Silyl Groups

Research Project

Project/Area Number

12650850

Research Category

Grant-in-Aid for Scientific Research (C)

Allocation Type

Single-year Grants

Section

一般

Research Field

Synthetic chemistry

Research Institution

Kanazawa University

Principal Investigator

SEGI Masahito Kanazawa University, Graduate school of natural science and technology, Assistant Professor, 自然科学研究科, 助教授 (90135046)

Co-Investigator(Kenkyū-buntansha)

HONDA Mitsunori Kanazawa University, Faculty of Engineering, Assistant Professor, 工学部, 助手 (60242533)

Project Period (FY)

2000 – 2001

Keywords

acylsilane / sulfur ylide / β -ketosilane / silylcarbinol / homoallyl ether / protodesilylation / asymmetric reduction / borane complex

Research Abstract

Reactions of acylsilanes with sulfur methylides proceed with cationotropy or anionotropy of silicon in the betaine intermediate to give the corresponding enolsilanes or β -ketosilanes. The product's ratio can be controlled by manipulating the reaction conditions. The reaction with sulfur ethylides and that with sulfur cyclopropylide result in the preferential formation of the corresponding α,β -epoxysilanes and cyclopropylidene(siloxy)methane derivatives, respectively. In contrast, various acylsilanes react with α -sulfinyl carbanions such as α -lithioalkyl phenyl sulfoxide to give the regiochemically pure enolsilanes produced by cationotropy of silicon to β -oxygen in the α -silyl- β -oxysulfoxide intermediate. The product's selectivity in these reactions depends on the leaving ability of sulfur compounds from the intermediate. In the reaction using sulfur ylides the elimination of neutral sulfur compound from the betaine intermediate occurs prior to the silicon migration, whereas in the reaction with α -sulfinyl

carbanions the cationotropy of silicon assists the elimination of sulfenate ion from the β -oxysulfoxide intermediate.

On the other hand, rearrangement of cyclopropylsilylcarbinols derived from cyclopropylacylsilanes with TsOH in methanol proceeds stereoselectively to give 4-silylhomoallyl methyl ether. The cyclopropylsilylcarbinols bearing n- or s-alkyl group on the carbonyl carbon produce E-4-silylhomoallyl methyl ethers, and those bearing f-butyl group afford Z-4-silylhomoallyl methyl ethers. E- and Z-4-silylhomoallyl methyl ethers are protodesilylated with TBAF to yield the corresponding Z- and E-olefins, respectively.

The asymmetric reduction of acylsilanes, in the presence of catalytic amounts of borane(-)-diphenylhydroxymethyl pyrrolidine complex, with borane leads to the corresponding optically active silylcarbinols in quantitative chemical yield and in high enantiomeric excess.

Research Products (6 results)

All Other

All Publications

[Publications] Shuji Tomoda: "Reversal of n-Facial Diastereoselection in the Hydride Reduction of Selenanones. Further Application of the Exterior Orbital Extention Model" *Tetrahedron Letters*. 41. 4597-4601 (2000) ▼

[Publications] Guang Ming Li: "On the Behavior of α , β -unsaturated Thioaldehydes and Thioketones in the Diels-Alder Reaction" *The Journal of Organic Chemistry*. 65. 6601-6612 (2000) ▼

[Publications] Mitsunori Honda: "Diastereoselective Aldol Condensation of Acylsilane Silyl Enol Ethers with Acetals" *Tetrahedron*. (発表予定). ▼

[Publications] Shuji Tomoda: "Reversal of n-Facial Diastereoselection in the Hydride Reduction of Selenanones. Further Application of the Exterior Orbital Extention Model" *Tetrahedron, Letters*. 41. 4597-4601 (2000) ▼

[Publications] Guang Ming Li: "On the Behavior of α , β -Unsaturated Thioaldehydes and Thioketones in the Diels-Alder Reaction" *The Journal of Organic Chemistry*. 65. 6601-6612 (2000) ▼

[Publications] Mitsunori Honda: "Diastereoselective Aldol Condensation of Acylsilane Silyl Enol Ethers with Acetals" *Tetrahedron*. (in press). ▼

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