

Retention of Configuration in the Ritter-type Substitution Reaction of Chiral β -Arylthio Alcohols through the Anchimeric Assistance of the Arylthio Group

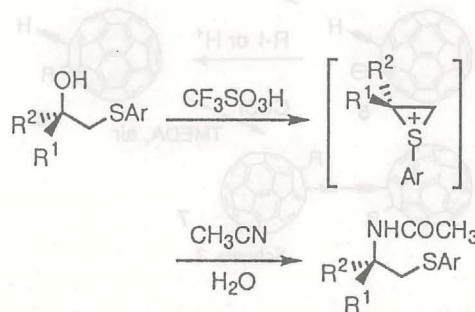
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In chiral alcohols bearing a phenylthio group at the β carbon atom, the hydroxy group is replaced by nitriles through the anchimeric assistance of the phenylthio group to afford chiral amides with retention of configuration. This stereospecific Ritter-type reaction has been utilized in the conversion of chiral glycidol derivatives to chiral cyclic imino ethers such as oxazolines bearing an arylthio group.

Keywords: Anchimeric assistance/ Arylthio group/ Ritter-type reaction/ Chiral amide/ Chiral oxazoline

Anchimeric assistance of the arylthio group has been widely observed in the substitution reactions at the carbon atom β to the arylthio group, the three-membered cyclic intermediate being known as an episulfonium ion. Diastereoselectivity, namely the erythro-threo selectivity has been established in the substitution reactions via the episulfonium ion. Enantioselectivity, i.e., the stereochemistry of the substitution reaction at the chiral carbon through the anchimeric assistance of the arylthio group (the stereochemical behavior of a chiral episulfonium ion), however, has not been studied so far [1]. We find that the chiral episulfonium ion does not racemize during the Ritter-type substitution reaction of the chiral β -phenylthio alcohols. Thus, chiral amides are produced with retention of configuration of the chiral carbon by the substitution of the hydroxy group by the nitrile through

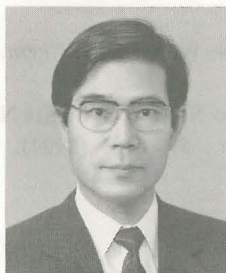
the anchimeric assistance of the phenylthio group. This result shows a sharp contrast to the behavior of the homologous chiral episelenonium ion which has recently been reported to racemize quite easily [2]. We have applied this Ritter-type reaction to chiral 1,2-diol



SYNTHETIC ORGANIC CHEMISTRY —Synthetic Design—

Scope of research

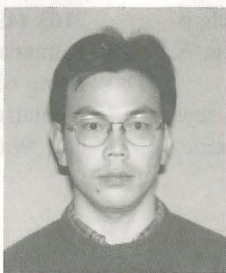
(1) Synthesis, structural studies, and synthetic applications of organosilicon compounds, such as pentacoordinated silicon compounds, functionalized silyl anions, and functionalized oligosilanes. (2) Design and synthesis of novel π -conjugated polymers containing silacyclopentadiene (silole) rings, based on new cyclization reactions and carbon-carbon bond formations mediated by the main group and transition metals. (3) Chiral transformations and asymmetric synthesis via organosulfur and selenium compounds, especially via chiral episulfonium and episelenonium ions.



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derivatives bearing the arylthio group to find that the intermediate iminium ion is trapped by the remaining hydroxy group to afford chiral cyclic imino ethers such as oxazolines.

The reaction described herein may be used as a new chiral pool method from readily accessible chiral oxiranes to chiral amine derivatives with retention of configuration of the chiral carbon [3].

References

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Oligosiloles: First Synthesis Based on a Novel *Endo-Endo* Mode Intramolecular Reductive Cyclization of Diethynylsilanes

Kohei Tamao and Shigehiro Yamaguchi

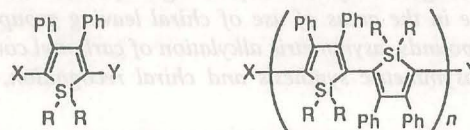
A general and versatile synthesis of 2,5-difunctionalized siloles is developed based on an *endo-endo* mode intramolecular reductive cyclization of diethynylsilanes upon treatment with lithium naphthalenide. With certain functionalized siloles in hand, oligosiloles, from bisiloles to quatersilole, are synthesized by oxidative coupling reaction via higher order cyanocuprates. Structural analysis and electronic properties of the oligosiloles have been investigated by means of X-ray crystallography, NMR studies, and UV-vis spectroscopy.

Keywords: 2,5-Difunctionalized silole/ Intramolecular reductive cyclization/ Oligosiloles/ Oxidative coupling reaction

Silole (silacyclopentadiene) containing π -conjugated polymers have recently been highlighted as a promising candidate for novel π -electronic materials, because of their anticipated properties such as conductivity, thermochromism, and nonlinear optical properties [1]. Polysiloles, silole-2,5-linked polymers, may be a center of target. Toward the polysilole synthesis, we succeeded in the first general and versatile synthesis of 2,5-difunctionalized siloles via a conceptually new intramolecular reductive cyclization of diethynylsilanes and the first synthesis of oligosiloles as models of the polysiloles by use of functionalized siloles in hand [2].

Bis(phenylethynyl)silane, $(\text{PhC}\equiv\text{C})_2\text{SiR}_2$ ($\text{R} = \text{Me}$, Et , $i\text{-Pr}$, and hexyl), underwent intramolecular reductive cyclization in an *endo-endo* mode upon treatment with lithium naphthalenide to form 2,5-dilithiosiloles **1**. This is the first example of intramolecular reductive cyclization of diynes proceeding in an *endo-endo* mode. The compounds **1** were converted into various 2,5-difunctionalized siloles, including 2,5-dibromosilole **2**, 5,5'-Dibromo-2,2'-bisilole **4** and 5,5'''-dibromo-2,2':5',2''-quatersilole **6**, were prepared by oxidative coupling via higher order cyanocuprate of 2-bromo-5-lithiosilole **3** and 5-bromo-5'-lithio-2,2'-bisilole **5**, respectively. X-ray crystal structures of the bisiloles show highly twisted arrangements between two silole

rings with torsion angle $62\text{--}63^\circ$. ^1H NMR studies on bisiloles show a rapid equilibration between noncoplanar conformers in solution. Despite the noncoplanar arrangement, all of the oligosiloles have unusually long absorption maxima in UV-vis spectra: λ_{max} (nm) in CHCl_3 ; bisilole **4**, 416; quatersilole **6**, 443. This remarkable electronic properties may be ascribed to an inherent unique electronic structures of silole ring. The present investigation on oligosiloles as models of polysiloles have enhanced our interests in the still veiled fascinating polysiloles.



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| 1 ($\text{X}=\text{Y}=\text{Li}$) | 4 ($\text{X}=\text{Y}=\text{Br}$, $n=1$) |
| 2 ($\text{X}=\text{Y}=\text{Br}$) | 5 ($\text{X}=\text{Br}$, $\text{Y}=\text{Li}$, $n=1$) |
| 3 ($\text{X}=\text{Br}$, $\text{Y}=\text{Li}$) | 6 ($\text{X}=\text{Y}=\text{Br}$, $n=2$) |

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