Diastereoselective Construction of Contiguous Chilal Centers by the Aldol Reaction of Acylsilane Silyl Enol Ethers.

1992 Fiscal Year Final Research Report Summary

Diastereoselective Construction of Contiguous Chilal Centers by the Aldol Reaction of Acylsilane Silyl Enol Ethers.

Research Project

Project/Area Number

03650694

Research Category

Grant-in-Aid for General Scientific Research (C)

Allocation Type

Single-year Grants

Research Field

Synthetic chemistry

Research Institution

KANAZAWA UNIVERSITY

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Project Period (FY)

1991 – 1992

Keywords

Silyl enol ether / Acylsilane / Aldol Reaction / Acetal / Stereoselective Reaction / Protiodesilylation

Research Abstract

There has been considerable interest in recent years in the stereoselective formation of multiple chiral centers using aldol reaction between prochiral enolates and aldehydes. We disclosed here an convenient method of diastereoselective construction of the three or four contiguous chiral centers using the Lewis acid mediated reaction of acylsilane silyl enol ethers (I) with acetals and the subsequent nucleophilic addition to the carbonyl group of the resulting acylsilanes (II).
Treatment of E-or Z-acylsilane silyl enol ethers (I) derived from acylsilanes having enolizable methylene proton with a mixture of aldehyde dimethylacetals and TiCl_4 in dichloromethane gave the corresponding 2,3-anti-3-methoxy-1-silyl-1-alkanones (II) in high diastereo excess,independent of the double bond

stereochemistry of I used. The similar reaction of E-I with d,1-phenylpropionealdehyde afforded 2,3-syn-3,4-syn-3-methoxy-1-silyl-1-butanal (V) in high stereoselectivity.
The resulting acylsilane 2,3-anti-II and 2,3-syn-3,4-syn-V were subjected to the nucleophilic reaction with alkyl or phenyllithium to yield the corresponding 3-methoxy-1-silyl-1-alkanols with three and four contiguous asymmetric centers (III and VI, respectively) stereoselectively. The protiodesilylation of III and VI with F^- reagent to afford the corresponding 1,2-anti-al- kanols with three and four contiguous asymmetric centers, IV and VII in 95-99% diastereo excess.

Research Products (6 results)

All | Other

All | Publications (6 results)

[Publications] Tadashi Nakajima: "Reaction of Acylsilanes with Meta-stable Phosphonium ylides and Phosphonium diylides." Bull.Chem.Soc.Jpn.

[Publications] Tadashi Nakajima: "Diastereoselective Construction of Three Contiguous Chiral Centers using Acylsilane Silyl Enol Ethers." Bull.Chem.Soc.Jpn.

[Publications] Tadashi Nakajima: "Diastereoselective Construction of Four Contiguous Chiral Centers by the Reaction of Acylsilane Silyl Enol Ethers with α-Chiral Aldehydeacetal." Chem.Lett.

[Publications] Tadashi Nakajima: "Reaction of Acylsilanes with Meta-stable Phosphonium ylides and Phosphonium diylides." Bull. Chem. Soc. Jpn.

[Publications] Tadashi Nakajima: "Diastereoselective Construction of Three Contiguous Chiral Centers using Acylsilane Silyl Enol Ethers." Bull. Chem. Soc. Jpn.

[Publications] Tadashi Nakajima: "Diastereoselective Construction of Four Contiguous Chiral Centers by the Reaction of Acylsilane Silyl Enol Ethers with a-Chiral Aldehydeacetal." Chem. Lett.

URL: https://kaken.nii.ac.jp/report/KAKENHI-PROJECT-03650694/036506941992kenkyu_seika_hokoku_

Published: 1994-03-23