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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

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Tamiko Takahashi^a; Noriyuki Kurose^a; Toru Koizijmi^a

^a Faculty of Pharmaceutical Sciences, Toyama Medical & Pharmaceutical University, Toyama, Japan

To cite this Article Takahashi, Tamiko , Kurose, Noriyuki and Koizijmi, Toru(1993) 'Molecular Designing of Chiral α -Alkoxy carbonylthioaldehydes and their Asymmetric Diels-Alder Reaction', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 74: 1, 367 – 368

To link to this Article: DOI: 10.1080/10426509308038118

URL: <http://dx.doi.org/10.1080/10426509308038118>

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MOLECULAR DESIGNING OF CHIRAL α -ALKOXYCARBONYLTHIO-ALDEHYDES AND THEIR ASYMMETRIC DIELS-ALDER REACTION

TAMIKO TAKAHASHI, NORIYUKI KUROSE and TORU KOIZUMI

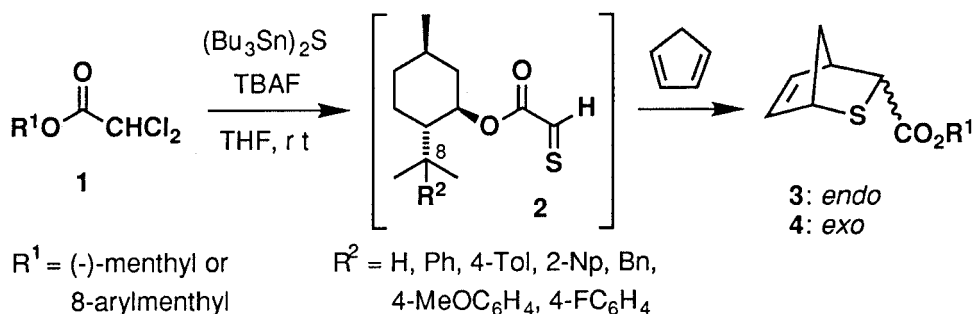
Faculty of Pharmaceutical Sciences, Toyama Medical & Pharmaceutical University, 2630 Sugitani, Toyama 930-01, Japan

Abstract High diastereoselectivity of the *endo* cycloaddition of optically active α -alkoxycarbonyl thioaldehydes (**2**) with cyclopentadiene is achieved by a molecular designing of the compound (**2**).

INTRODUCTION

Compounds having a carbon-chalcogen double bond are very attractive substrates because of their high reactivity. Recently, efficient synthetic methods of these unstable compounds have been developed. In the presence of a diene, the resulting chalcogeno-carbonyl compounds are trapped as Diels-Alder adducts. However, little attention has been focused on the application of such reactions to synthetic organic chemistry, especially to an asymmetric synthesis.¹ We thus proceeded to a utilization of chiral thioaldehydes to an asymmetric reaction.

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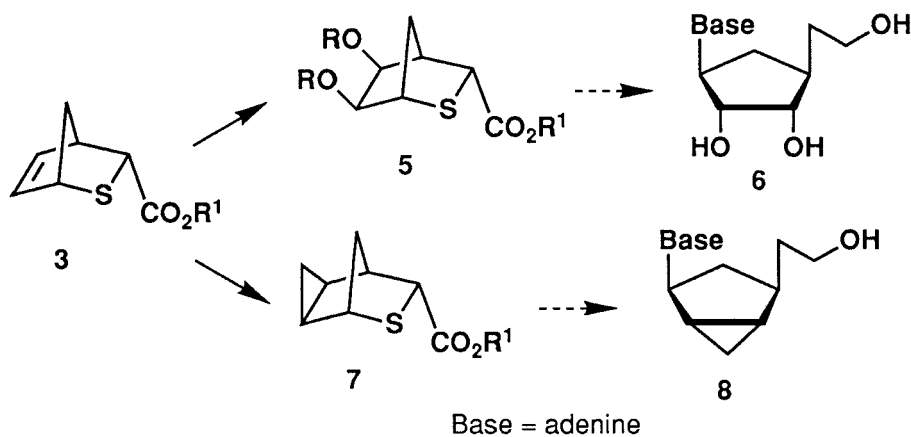
Chiral thioaldehydes (**2**) were prepared from the corresponding α -dichloroacetates (**1**) and S^{2-} which was generated by a fluorodestannylation reaction of bis(tributyltin)sulfide

with tetrabutylammonium fluoride (TBAF).² These thioaldehydes reacted immediately with cyclopentadiene to give the cycloadducts (**3** and **4**). The diastereomer excess (d.e.) of the *endo* cycloadducts (**3**) increased from 14% to 80% by replacing (-)-menthyl group ($R^2 = H$) with (-)-8-phenylmenthyl group ($R^2 = Ph$).

Such high diastereoselectivity of the *endo* cycloaddition with 8-phenylmenthyl derivative (**2**; $R^2 = Ph$) would be explained as follows: block of the *si*-face of thiocarbonyl carbon of **2** by interaction with the phenyl group³; diene attack to the *re*-face of the carbon. To obtain higher diastereoselectivity, we designed various chiral α -menthyloxy-carbonylthioaldehydes having a *p*-substituted 8-aryl group. As a result, the diastereoselectivity of the *endo* cycloaddition was the highest (84% d.e.) in the case of 4-tolyl group (**2**; $R^2 = 4\text{-Tol}$).

APPLICATION OF THE *ENDO* CYCLOADDUCT TO A CHIRAL SYNTHESIS OF (+)-5'-HOMOARISTEROMYCIN AND ITS ANALOGUE

An application of the asymmetric Diels-Alder reaction to a chiral synthesis of (+)-5'-homoaristeromycin (**6**)⁴ and its analogue (**8**) is now under investigation and the details would be presented.



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