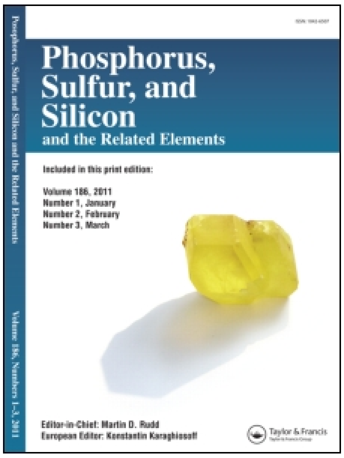


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Molecular Designing of Chiral α-Alkoxycarbonylthioaldehydes and their Asymmetric Diels-Alder Reaction

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-Alkoxycarbonylthioaldehydes 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

Phosphorus, Sulfur, and Silicon, 1993, Vol. 74, pp. 367–368
Reprints available directly from the publisher
Photocopying permitted by license only

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

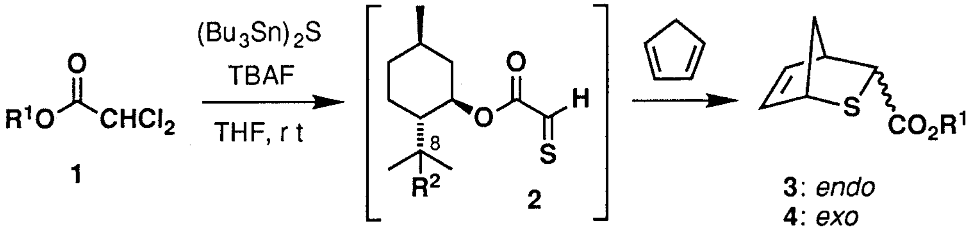
TAMIKO TAKAHASHI, NORIYUKI KUROSE and TORU KOIZUMI
Faculty of Pharmaceutical Sciences, Toyama Medical & Pharmaceutical University, 2630 Sugitani, Toyama 930-01, Japan

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 chalcogenocarbonyl 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.

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



R^1 = (-)-menthyl or 8-arylmenthyl

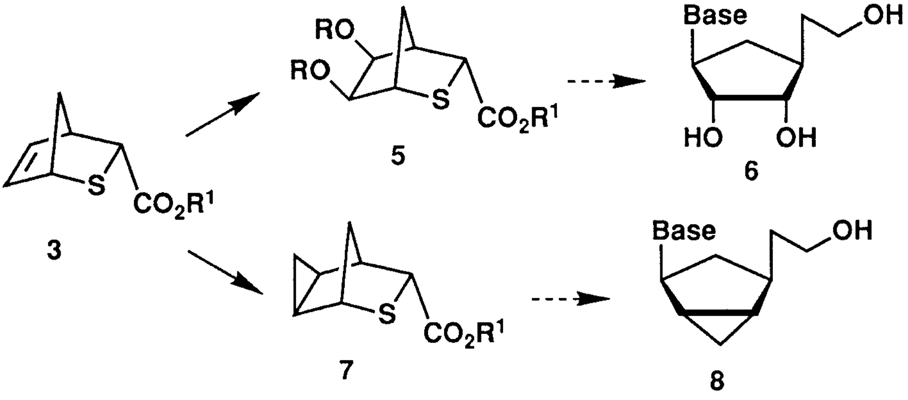
R^2 = H, Ph, 4-Tol, 2-Np, Bn, 4-$MeOC_6H_4$, 4-FC_6H_4

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 group[3]; diene attack to the *re*-face of the carbon. To obtain higher diastereoselectivity, we designed various chiral α-menthyloxycarbonylthioaldehydes 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-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.



Base = adenine

REFERENCES

1. E. Vedejs, J. S. Stults and R. G. Wilde, J. Am. Chem. Soc., 110, 5452 (1988).
2. M. Segi, M. Kato and T. Nakajima, Tetrahedron Lett., 32, 7427 (1991).
3. W. Oppolzer, C. Robbiani and K. Bättig, Helv. Chim. Acta, 63, 2015 (1980).
4. M. F. Jones and S. M. Roberts, J. Chem. Soc. Perkin Trans. 1, 2927 (1988).