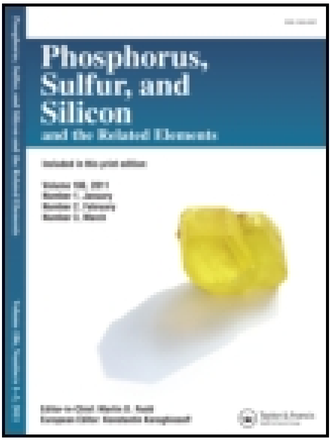

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Asymmetric Induction by a Sulfinyl Group in the Thio-Claisen Rearrangement

Carole Alayrac , Stephanie Nowaczyk , Margareth Lemarie & Patrick Metzner

[a] Laboratoire de Chimie Moléculaire et Thio-organique (UMR n° 6507 CNRS) ISMRA - Université , 6 boulevard du Maréchal Juin, 14050 Caen, France

[b] Laboratoire de Chimie Moléculaire et Thio-organique (UMR n° 6507 CNRS) ISMRA - Université , 6 boulevard du Maréchal Juin, 14050 Caen, France

[c] Laboratoire de Chimie Moléculaire et Thio-organique (UMR n° 6507 CNRS) ISMRA - Université , 6 boulevard du Maréchal Juin, 14050 Caen, France

[d] Laboratoire de Chimie Moléculaire et Thio-organique (UMR n° 6507 CNRS) ISMRA - Université , 6 boulevard du Maréchal Juin, 14050 Caen, France

To cite this article: Carole Alayrac , Stephanie Nowaczyk , Margareth Lemarie & Patrick Metzner (1999) Asymmetric Induction by a Sulfinyl Group

in the Thio-Claisen Rearrangement, Phosphorus, Sulfur, and Silicon and the Related Elements, 153:1, 317-318, DOI: 10.1080/10426509908546449

To link to this article: http://dx.doi.org/10.1080/10426509908546449

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Phosphorus, Sulfur and Silicon, 1999, Vol. 153-154, pp. 317-318
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Gordon and Breach Science Publishers imprint.
Printed in Malaysia

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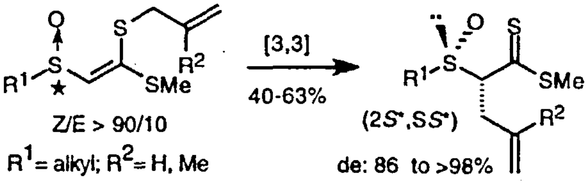
CAROLE ALAYRAC, STEPHANIE NOWACZYK,
MARGARETH LEMARIE and PATRICK METZNER

Laboratoire de Chimie Moléculaire et Thio-organique (UMR n° 6507 CNRS)
ISMRA – Université, 6 boulevard du Maréchal Juin, 14050 Caen, France

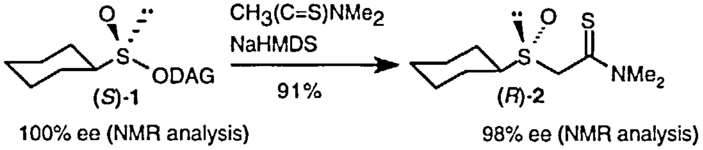
The first examples of an asymmetric thio-Claisen rearrangement induced by an enantiopure alkylsulfinyl group are reported.

Keywords: chiral auxiliaries; rearrangement; thiocarbonyl; sulfoxide

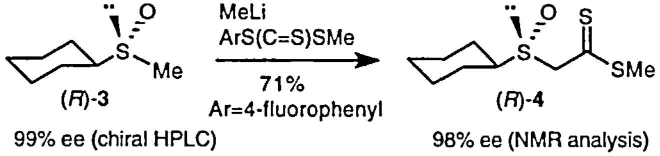
The Claisen rearrangement is well established as an important method for the stereoselective formation of C-C bonds in acyclic systems. However only a few asymmetric variants involving a removable chiral auxiliary are known.[1] We recently reported the first examples of an asymmetric [3,3] sigmatropic rearrangement stereocontrolled by a racemic alkylsulfinyl group:[2]



In order to apply our method to enantiopure substrates, we wished to synthesise optically active 2-alkylsulfinyl dithioesters and thioamides. The most straightforward route is the reaction of a chiral sulfinate with an enethiolate. Such reaction is not known with dithioester enolates. The diastereoselective synthesis of chiral alkyl sulfinates from diacetone-(*D*)-glucose (DAG) was recently reported.[3] By analogy, we prepared previously unreported (*S*)-DAG cyclohexanesulfinate **1** from racemic cyclohexanesulfinyl chloride (46%). Its reactivity towards enethiolates was examined. The sodium thioamide enolate proved to be much more reactive than the lithium one and afforded thioamide **2** with 91% yield and 98% ee.



Our attempts to prepare dithioester **4** under the same conditions failed. Finally it was obtained from enantiopure sulfoxide **3** resulting from the reaction of **1** with a Grignard reagent.[3]



The thio-Claisen rearrangement of the enantiopure substrates was achieved with similar diastereoselectivities as those observed with the racemic substrates. Thus, the control of relative and absolute stereochemistry is possible by this method.

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