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

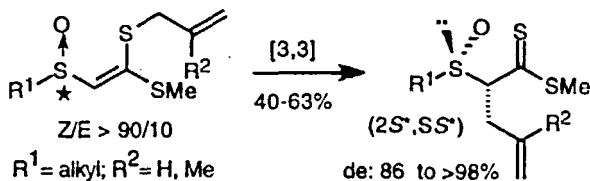
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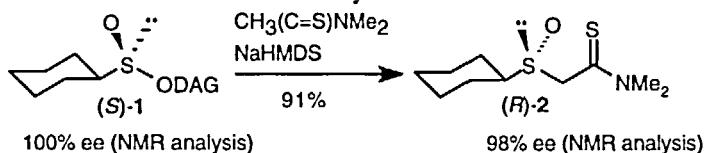
The first examples of an asymmetric thio-Claisen rearrangement induced by an enantiopure alkylsulfinyl group are reported.

Keywords: chiral auxiliaries; rearrangement; thiocarbonyl; sulfoxide

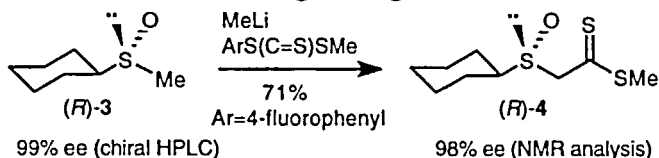
The Claisen rearrangement is well established as an important method for the stereoselective formation of C-C bonds in acyclic systems. However only a few asymmetric variants involving a removable chiral auxiliary are known.^[1] We recently reported the first examples of an asymmetric [3,3] sigmatropic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

References

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