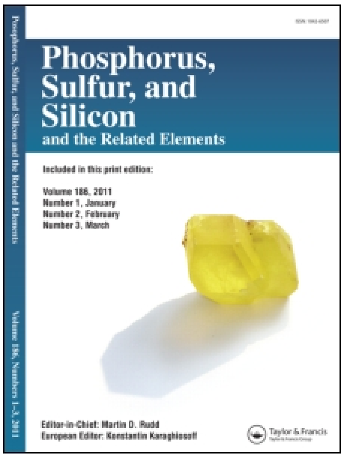

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The First Examples of a Claisen Rearrangement Stereocontrolled by a Sulfur Center of Chirality

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The First Examples of a Claisen Rearrangement Stereocontrolled by a Sulfur Center of Chirality

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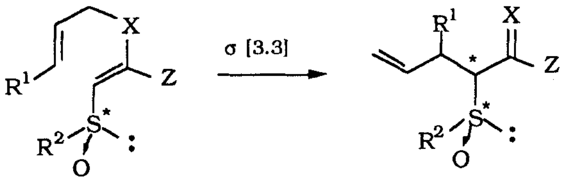
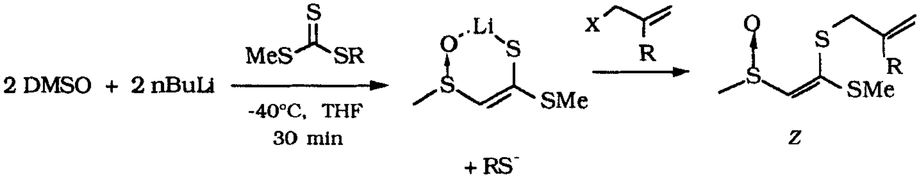
The asymmetric version of the Claisen rearrangement (1) usually involves the preparation of a carboxylic ester of an **enantiomerically pure allylic alcohol**, its deprotonation and transposition either of the lithium enolate or its silyl ketene acetal.

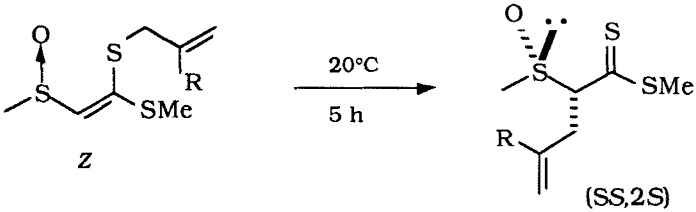
We have wished to explore a novel way: introduction of an auxiliary of chirality. We have chosen a sulfinyl group. The unsaturated sulfoxides have been used with success for the stereocontrol of Diels-Alder cycloadditions (Koizumi, Maignan, De Lucchi) and Michael additions (Posner). To our knowledge their application to a diastereoselective Claisen rearrangement has not been reported. One obvious limit is the easy elimination of sulfenic acid from the product under thermal conditions (2). To avoid it we decided to carry out the rearrangement in the sulfur series (X = S) which might occur under mild conditions: the group of Brandsma (3) and later ours (4) have shown that replacement of an oxygen atom by sulfur brings about a decrease of at least 5 kCal/mol for the activation enthalpy. A number of examples demonstrate the advantages of the thio-Claisen transposition (5).



We wish to report our first approach, achieved in the racemic series. According to Yokoyama *et al* (6) we have treated lithiated DMSO with methyl phenyl trithiocarbonate to afford methyl 2-methylsulfinylethanedithioate, which was subsequently deprotonated and S-allylated to give access to the expected ketene dithioacetal.



To our delight this compound rearranged **at ambient temperature** and the allylated dithioester was obtained with a diastereomeric ratio of **93** : **7** (R = H) or **94** : **6** (R = Me) with overall yields from 50 to 63%. A crystallographic study revealed that the major isomer has a (*S*S, 2*S*) structure.



A model is proposed involving an s-*trans* conformation for the α-unsaturated sulfoxide moiety and an attack of the allyl part from the more electron rich and less hindered face (bearing the sulfur lone pair) of the ketene dithioacetal, both parameters being matched.

Preliminary results on the rearrangement of an *S*-crotyl ketene dithioaccetal revealed a promising diastereoisomeric ratio of 86 : 11 : 2 : 1. Assignment of the configuration of the major isomer and applications of the above results to enantiopure sulfoxides are under investigation.

References

1. R. K. Hill, in *Asymmetric Synthesis*, edited by J. D. Morrison (Academic Press, New-York, 1984), Vol. 3, Part B, p. 503. S. Pereira and M. Srebnik, *Aldrichimica Acta*, **26**, 17 (1993).
2. G. H. Posner and C. M. Kinter, *J. Org. Chem.*, **55**, 3967 (1990).
3. P. J. W. Schuijl and L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, **87**, 929 (1968). P. J. W. Schuijl, H. J. T. Bos, and L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, **88**, 597 (1969).
4. P. Metzner, T. N. Pham, and J. Vialle, *Nouv. J. Chim.*, **2**, 179 (1978).
5. P. Metzner, *Synthesis*, 1185 (1992). P. Metzner and A. Thuillier, *Sulfur Reagents in Organic Synthesis* (Academic Press, Londres, 1994), in the press. S. Désert, P. Metzner, and M. Ramdani, *Tetrahedron*, **48**, 10315 (1992). P. Beslin and S. Perrio, *Tetrahedron*, **47**, 6275 (1991). P. Beslin and S. Perrio, *Tetrahedron*, **48**, 4135 (1992).
6. M. Yokoyama, K. Tsuji, M. Hayashi, and T. Imamoto, *J. Chem. Soc., Perkin Trans. 1*, 85 (1984).