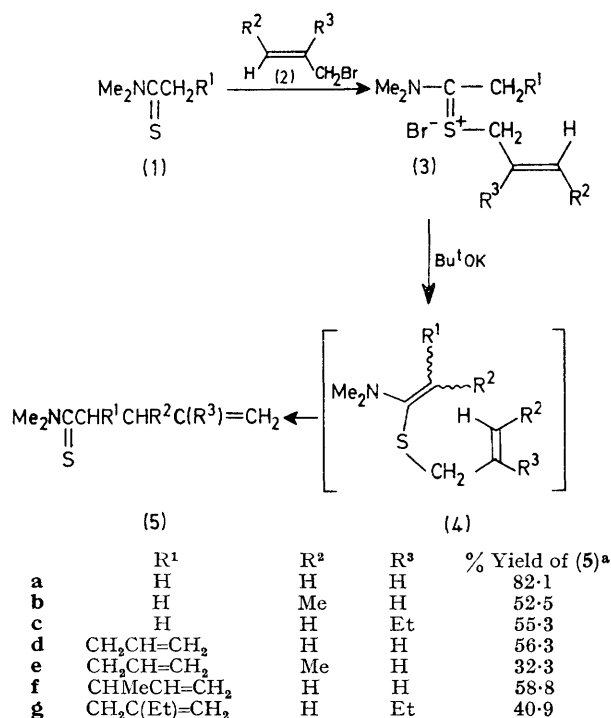


## New Synthetic Route to Mono- and Di- $\gamma\delta$ -Unsaturated *NN*-Dialkylthioamides by the Thio-Claisen Rearrangement Based on Acyclic *NN*-Dialkylthioamides

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**Summary** Mono- and di- $\gamma\delta$ -unsaturated *NN*-dialkylthioamides have been synthesized by a thio-Claisen rearrangement of  $\alpha$ -amino- $\alpha\beta$ -unsaturated sulphides derived from acyclic *NN*-dialkylthioamides.



<sup>a</sup> Overall yield from (1) after purification by preparative t.l.c.

† Satisfactory analytical and spectral data were obtained for all new compounds except the unstable sulphonium salts.

<sup>1</sup> There are two reports on the thio-Claisen rearrangement of  $\alpha$ -amino- $\alpha\beta$ -unsaturated sulphides obtained from different sources: P. S. W. Schuijl and L. Brandsma, *Rec. Trav. chim.*, 1968, **87**, 929; T. Sasaki, A. Kojima, and M. Ohta, *J. Chem. Soc. (C)*, 1971, 196.

<sup>2</sup> D. Felix, K. Gschwend-Steen, A. E. Wick, and A. Eschenmoser, *Helv. Chim. Acta*, 1969, **52**, 1030.

<sup>3</sup> W. S. Johnson, L. Werthemann, W. R. Bartlett, T. J. Brocksom, T.-t. Li, D. J. Faulkner, and M. R. Petersen, *J. Amer. Chem. Soc.*, 1970, **92**, 741.

To our knowledge, there has been no report on the thio-Claisen rearrangement of  $\alpha$ -amino- $\alpha\beta$ -unsaturated sulphides<sup>1</sup> derived from acyclic thioamides. We now report the first example of the thio-Claisen rearrangement based on acyclic *NN*-dialkylthioamides which can be applied to the synthesis of mono- and di- $\gamma\delta$ -unsaturated *NN*-dialkylthioamides<sup>†</sup> and related compounds. The method involves simply stirring the sulphonium bases (3), obtained from the *NN*-dialkylthioamides (1) and allyl bromides (2), with 1.0–1.2 mol. equiv. of KOBu<sup>†</sup> in tetrahydrofuran at room temperature. Presumably the  $\alpha$ -amino- $\alpha\beta$ -unsaturated sulphides (4) are first formed which rearrange to the  $\gamma\delta$ -unsaturated thioamide (5).

In comparison with both the Eschenmoser<sup>2</sup> and Johnson<sup>3</sup> versions of the Claisen rearrangement, this thioamide process is more favourable for repeating the rearrangement to introduce a second  $\gamma\delta$ -unsaturated alkyl group (in principle it can be carried out as many times as there are  $\alpha$ -hydrogen atoms in the thioamides, though we did not succeed in carrying out the third reaction) without changing the functional group.

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