New Synthetic Route to Mono- and Di-γδ-Unsaturated *NN*-Dialkylthioamides by the Thio-Claisen Rearrangement Based on Acyclic *NN*-Dialkylthioamides

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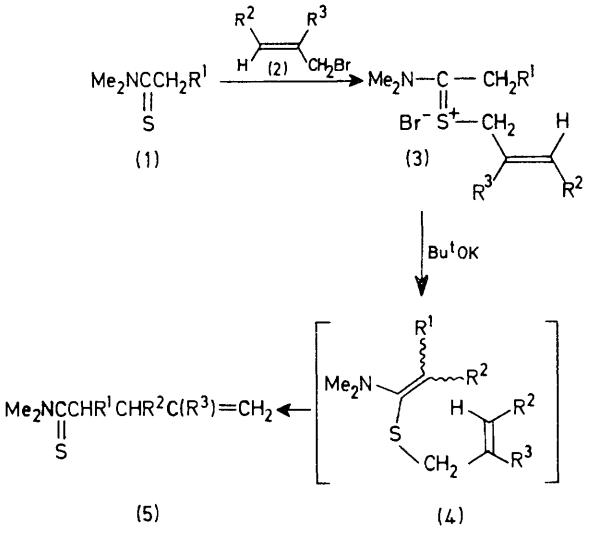
Summary Mono- and di-γδ-unsaturated *NN*-dialkylthioamides have been synthesized by a thio-Claisen rearrangement of α-amino-αβ-unsaturated sulphides derived from acyclic *NN*-dialkylthioamides.



	R^1	R^2	R^3	% Yield of (5)[a]
a	H	H	H	82·1
b	H	Me	H	52·5
c	H	H	Et	55·3
d	$CH_2CH{=}CH_2$	H	H	56·3
e	$CH_2CH{=}CH_2$	Me	H	32·3
f	$CHMeCH{=}CH_2$	H	H	58·8
g	$CH_2C(Et){=}CH_2$	H	Et	40·9

[a] Overall yield from (**1**) after purification by preparative t.l.c.

To our knowledge, there has been no report on the thio-Claisen rearrangement of α-amino-αβ-unsaturated sulphides[1] 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-γδ-unsaturated *NN*-dialkylthioamides† 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 $KOBu^t$ in tetrahydrofuran at room temperature. Presumably the α-amino-αβ-unsaturated sulphides (**4**) are first formed which rearrange to the γδ-unsaturated thioamide (**5**).

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

(*Received, 28th June* 1976; *Com.* 721.)

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

[1] There are two reports on the thio-Claisen rearrangement of α-amino-αβ-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.

[2] D. Felix, K. Gschwend-Steen, A. E. Wick, and A. Eschenmoser, *Helv. Chim. Acta*, 1969, **52**, 1030.

[3] 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.