

THIOAMIDE-CLAISEN REARRANGEMENTS AND ITS APPLICATION TO
THE SYNTHESIS OF INDOLE ALKALOIDS

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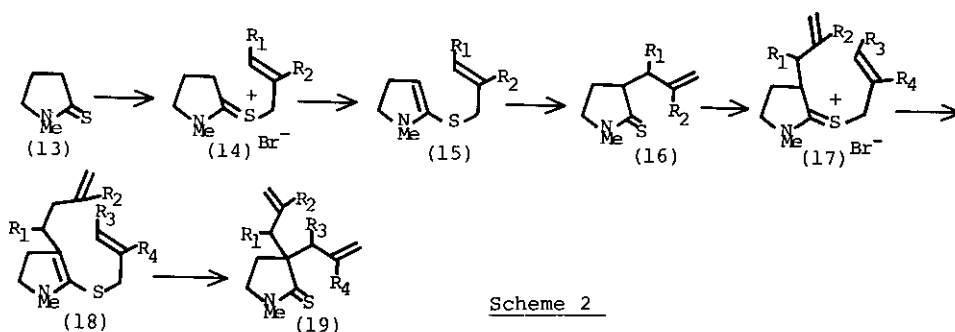
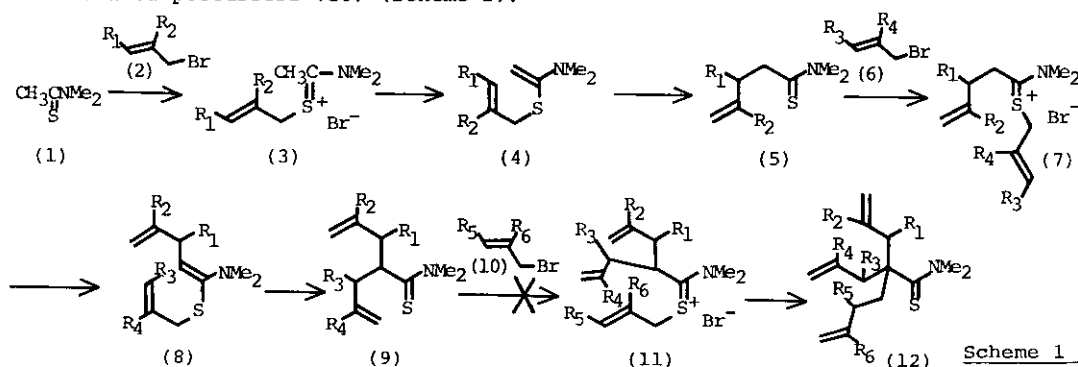
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Using an acyclic (1) and a cyclic (13) thioamides as substrates, thio-Claisen rearrangement reaction has been examined.

In the acyclic substrate, the rearrangement can be reiterated to give di- γ,δ -unsaturated thioamides (9) via mono- γ,δ -unsaturated precursors (5), but further iteration forming quaternary α -center cannot be achieved because of unreactivity of the α,α -disubstituted compounds to allyl bromides due to steric hindrance (Scheme 1).

On the other hand, in the cyclic substrate, the rearrangement can be reiterated to give di- γ,δ -unsaturated thioamides with quaternary α -center (19) via mono- γ,δ -unsaturated precursors (16) (Scheme 2).



Employing the thio-Claisen rearrangement reaction as a key stage, a new synthetic approach to some indole alkaloids have been developed.