HETEROCYCLES, Vol 20, No 1, 1983

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

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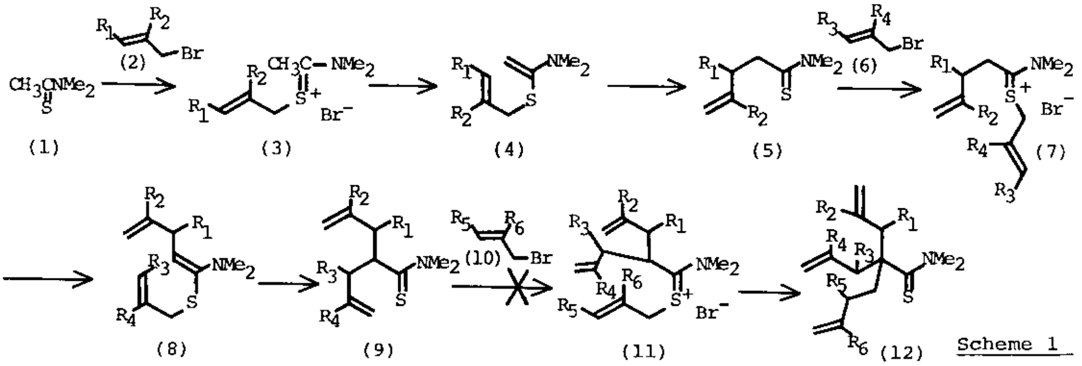
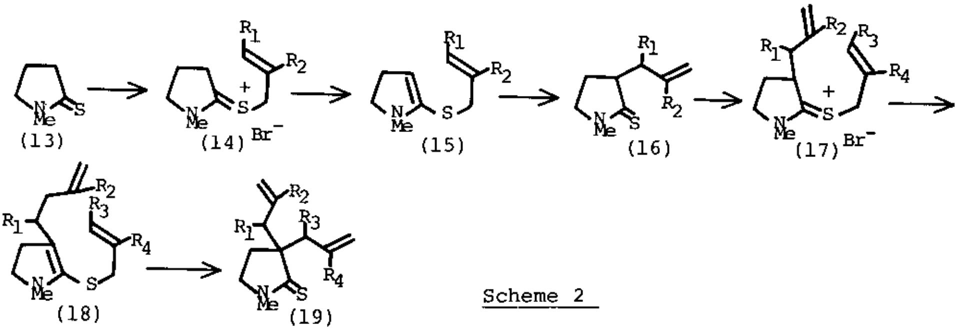
Using an acyclic (1) and a cyclic (13) thioamides as substrates, thio-Claisen rearrangement reaction has been examined.

In the acyclic substrate, the rearrangement can be reiterated to give di-γ,δ-unsaturated thioamides (9) <u>via</u> 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) <u>via</u> mono-γ,δ-unsaturated precursors (16) (Scheme 2).



Scheme 1



Scheme 2

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