Thio-Claisen Rearrangements of Allyl and Prop-2-ynyl 2-Indolyl Sulphides

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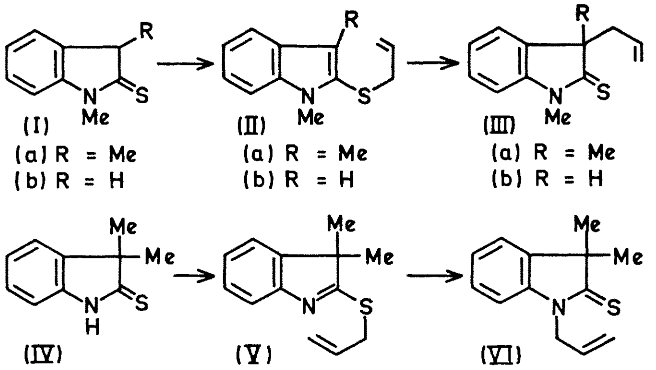
Summary Thermal rearrangement of allyl and prop-2-ynyl 2-indolyl sulphides is shown to proceed *via* a 3,3-sigmatropic process.

OUR interest in natural products derived from the interaction of tryptophan and a C_5 unit led us to consider the possible utility of thio-Claisen rearrangements in a general synthetic approach to this class of compounds. This type of rearrangement has received relatively little attention.[1-3]

The thiones (Ia, Ib, and IV) were prepared from the corresponding oxindoles by the method of Hino.[4] Reaction with allyl bromide in acetone over anhydrous potassium carbonate afforded, in high yield, the thio-ethers (IIa, IIb, and V). Similarly, the thio-ether (VIIa) was prepared from (Ib) and prop-2-ynyl bromide.



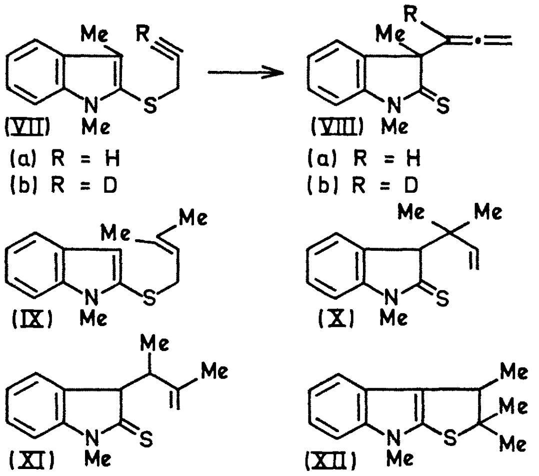
Rearrangement of (IIa, IIb, and VIIa) to the thiones (IIIa, IIIb, and VIIIa) respectively, occurred readily on heating them in polar or non-polar solvents but was most conveniently achieved in toluene under reflux. The thermolysis of (V) to (VI), however, could only be effected in tetralin under reflux. In all these reactions the yields were virtually quantitative and the products fully characterised. Furthermore, the products showed no tendency to cyclise, as had been previously observed with related compounds.[1-3]

The formation of the thiones could be followed by u.v. spectroscopy and from the first-order rate constants obtained at a number of different temperatures, the energies and entropies of activation were derived for some of these reactions (see Table). The activation energies are comparable with those obtained by Brandsma[3a] on a related series of thio-ethers and the data are consistent with these reactions following concerted pathways. The low negative entropy of activation for the rearrangement of (VIIa) can be accounted for in terms of the increased rigidity imposed on a six-centred transition state.

Thermal rearrangement of thio-ethers

Compound	$\Delta E\ddagger$ (kcal./mole)	$\Delta S\ddagger$ (e.u.)
(Ia)	18·6	−19·4
(Ib)	19·2	−16·8
(VIIa)	23·8	−6·3

Verification that the exclusive course of the reaction (VIIa → VIIIa) is as expected was obtained as follows. Thermolysis of (VIIb), prepared from (Ib) and [3-^{2}H]-prop-2-ynyl bromide,[5] afforded the allene (VIIIb), the n.m.r. spectrum of which clearly demonstrated that it possessed the structure shown and that there had been no scrambling of the deuterium.



Experiments with alkyl-substituted allyl sulphides have confirmed that these are also 3,3-sigmatropic[6,7] processes. The thio-ether (IX) on standing at room temperature slowly equilibrates to a mixture of (IX) and (X). The C_5 unit in (X) is clearly present as $CMe_2{\cdot}CH:CH_2$; τ 8·65 (s, 3H),) 9·0 (s, 3H), and three vinylic protons which can be assigned to $-CH:CH_2$. Attempts to increase the yield of (X) by heating (IX) were unsuccessful and resulted in the formation of the abnormal rearrangement product (XI) and the corresponding ring-closed derivative (XII).

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