Claisen Rearrangement of *O*-Allyl and *O*-Cinnamyl Imino-esters of Hexanolactam

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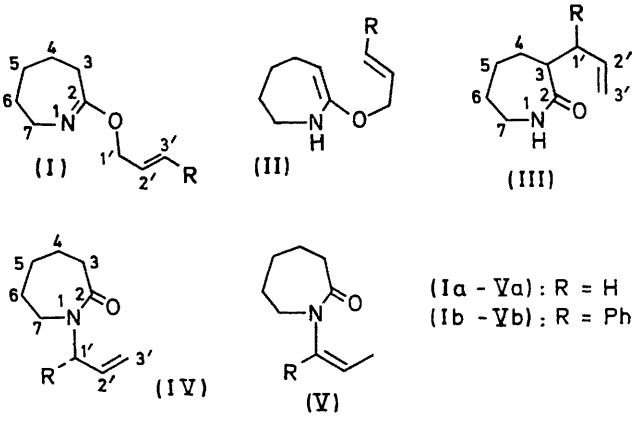
Summary *O*-Allyl and *O*-cinnamyl imino-esters of hexanolactam undergo Claisen rearrangement at about 210° on to C-3 in preference to the nitrogen atom.

WE report that *O*-allylhexanolactim (Ia) (b.p. 206°/760 mm Hg) undergoes thermal rearrangement, on heating at 210—212° for 13 h in a sealed tube, predominantly to 3-allylhexanolactam (IIIa),† m.p. 87° (60% yield), $C_9H_{15}NO$, *m/e* 153, together with a small amount of 1-allylhexanolactam (IVa).

Reaction of *O*-methylhexanolactim[1] with allyl alcohol at 110—120° for 18 h afforded *O*-allylhexanolactim‡ (Ia), b.p. 88—92°/20 mm Hg (32% yield).

The 1-allylhexanolactam (IVa) was detected by ^{1}H n.m.r. spectral comparison of the crude reaction product with an authentic specimen (b.p. 76—78°/0·1 mm) prepared[2] by reaction of allyl bromide with the sodium salt of hexanolactam. The C-1′ protons of (IVa) resonate as a doublet at 4·00 p.p.m. downfield from Me_4Si (*J* 6 Hz), thus providing a very clear spectral marker. Neither (IIIa) nor (IVa) rearrange on further heating.

The intramolecular nature of the rearrangement was confirmed by the similar conversion of *O*-cinnamylhexanolactam (Ib) at 212—214° to (IIIb), m.p. 116—117°, *m/e* 229.



In the above rearrangement of (Ib), a trace of (Vb) was detected by ^{1}H n.m.r. spectroscopy: this product (Vb) presumably arose by ready isomerisation of (IVb). In

† Satisfactory i.r. and ^{1}H n.m.r. ($CDCl_3$; 60 MHz) spectral data were obtained for all compounds described.
‡ First isolated in this laboratory by A. J. Poynton.

contrast, the allyl derivative (IVa) was not converted into (Va) under the above reaction conditions.

Treatment of (Ia) and (Ib) at higher temperatures leads to an increase in the proportion of products resulting from rearrangement on to nitrogen. Initial bond migration of (I) into (II) is required for rearrangement on to carbon and the nature of this isomerisation is being investigated. It would appear, however, that rearrangement of (II) to (III) requires a lower activation energy than rearrangement of (I) to (IV).

Similar Claisen rearrangements have been observed in fully-alkylated keten-acetals[3] and their nitrogen[4] and sulphur[5] analogues, where there is no possibility of bond isomerisation. The results described above provide an important extension of the synthetic potential of the Claisen rearrangement. The generality of this process is under current investigation, with particular reference to the variability of size of the lactam ring, and extension to thioether analogues and oxindole derivatives.

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