Thermal Sigmatropic Rearrangement of 3-Allylindolenines to Indoles and of a 4-Allylisopyrazole to a Pyrazole

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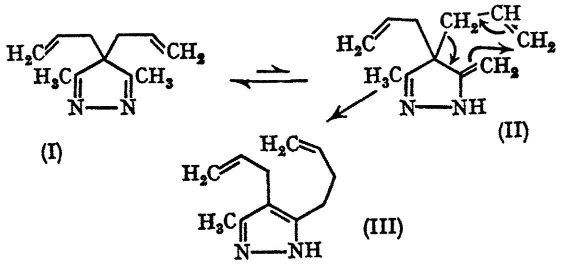
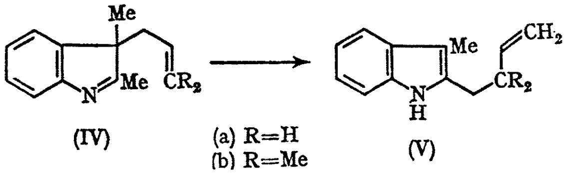
THE recent publication of Hill and Newkome[1] on the thermal rearrangement of *N*-allyl anhydro-bases prompts us to record our investigations of a related reaction. The 4,4-diallyl-3,5-dimethylisopyrazole (I) was prepared (91%) from hydrazine and the β-diketone in the normal way. The n.m.r. spectrum of (I) showed no evidence of the enamine tautomer (II) but ready deuterium exchange of the 3- and 5-methyl groups occurred in D_2O–NaOD–pyridine at room temperature.

The thermal rearrangement of (I) was investigated to ascertain which of the several possible sigmatropic rearrangement routes was preferred. Rearrangement occurred smoothly (quantitative by t.l.c., 88% isolated) in boiling xylene (5½ hr.). The product was a pyrazole, and n.m.r. evidence clearly indicated that the structure was (III). Thus a [3,3] sigmatropic rearrangement had occurred *via* the enamine (II → III; arrows).

An analogous series of rearrangements has been studied in the indolenine system. The 3-allylindolenines (IV) and (VI) were prepared from the indole Grignard reagent and the appropriate allyl bromide. Rearrangement of the indolenine (IVa) to the indole (Va) was achieved in refluxing *o*-dichlorobenzene (15 hr.) or in boiling tetralin (6¼ hr.; 89% isolated). To demonstrate the inversion of the allyl group required by a [3,3]-sigmatropic shift the rearrangement of the indolenines (IVb) and (VI) was investigated.

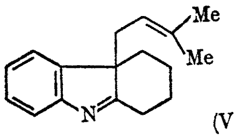


(I) (II) (III)

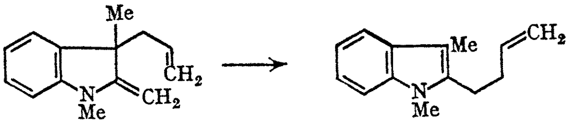


(IV) (a) R=H (b) R=Me (V)

The indolenine (IVb) rearranged to some extent in *o*-dichlorobenzene but more rapidly in boiling tetralin (3½ hr.) to the indole (Vb) together with some 2,3-dimethylindole, while (VI) required more vigorous conditions (refluxing 1-chloronaphthalene) and gave a mixture of products still under investigation.



(VI)



(VII) (VIII)

It seemed that the temperature required to effect these rearrangements might be considerably lowered by converting the ketimine into the enamine prior to the rearrangement. Thus the methiodide of (IVa) was prepared and converted into the enamine (VII) by action of sodium hydroxide. The thermal rearrangement of this enamine occurred very slowly in boiling benzene and was more conveniently carried out in toluene (110°) when the expected indole (VIII) was obtained.

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[1] R. K. Hill and G. R. Newkome, *Tetrahedron Letters*, 1968, 5059.