The Base-catalysed Isomerisation of 2-Acetylimino-3-phenacylthiazolidine

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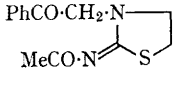
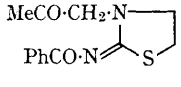
DURING synthetic studies on 2-aminothiazoline derivatives, a ready rearrangement of 2-acetylimino-3-phenacylthiazolidine (I)[1,2] into the isomeric 2-benzoylimino-3-(propan-2-onyl)thiazolidine (II) was observed in a variety of basic media. An almost quantitative conversion takes place merely on refluxing with sodium acetate in ethanol. The isomeric compound (II) (m.p. 92°, *ex* aqueous ethanol) exhibited a strong carbonyl absorption at 1720 cm.$^{-1}$ and weaker bands at 1625 cm.$^{-1}$ and 1615 cm.$^{-1}$ in its infrared spectrum (Nujol). The 60 Mc./sec. n.m.r. spectrum ($CDCl_3$ solution) indicated the presence of five aromatic protons (multiplets at τ 1·75 to 1·9 and τ 2·45 to 2·8), the $-CH_2-CH_2-$ system (A_2X_2 triplets at τ 6·1 to 6·4 and τ 6·6 to 6·9), a methylene group (singlet τ 5·5) and a methyl group (singlet τ 7·8). Reduction of (II) with sodium borohydride in ethanol furnished the alcohol (III) (m.p. 91°—92° *ex* toluene), which showed bands at 3510 cm.$^{-1}$, 1610 cm.$^{-1}$ and 1600 cm.$^{-1}$ in its infrared spectrum (Nujol). The 100 Mc./sec. n.m.r. spectrum ($CDCl_3$ solution shaken with D_2O) revealed the presence of five aromatic protons (multiplets at τ 1·75 to 1·95 and τ 2·5 to 2·8), a $\geqslant$CH group (multiplet at τ 5·7 to 6·0), a methylene group (part of multiplet at τ 6·2 to 6·5), the $-CH_2-CH_2-$ system [triplets at τ 6·2 to 6·5 (part of multiplet) and τ 6·9 to 7·15] and a methyl group (doublet at τ 8·8 and 8·85). Spin decoupling of the methyl group caused the $\geqslant$CH multiplet to collapse to two doublets representing the X part of an ABX system.

Synthetic verification for the structure of the isomerisation product was provided by condensation of 2-aminothiazoline with chloroacetone to give 2-imino-3-(propan-2-onyl)thiazolidine hydrochloride, which when treated with benzoyl chloride in pyridine furnished a compound identical in every respect with the rearrangement product.

A preliminary investigation of the reaction path suggests the involvement of the diketone (IV), formed *via* the carbanion generated from (I), as a transient intermediate. Treatment of 1-bromobenzoylacetone[3] with two equivalents of 2-aminothiazoline furnished almost one equivalent of 2-aminothiazoline hydrobromide and a brown oil, which on chromatography (1 mm. silica plates, eluent ether) produced (I) and (II) in 13% and 50% yields respectively. All attempts to isolated the hydrobromide of (IV) failed. Extensions of this base-catalysed isomerisation to other systems and its utilisation in heterocyclic syntheses are in progress.



(I)



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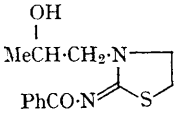
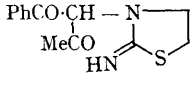


(III)



(IV)

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[3] F. Krohnke and H. Timmler, *Ber.*, 1936, **69**, 614.