

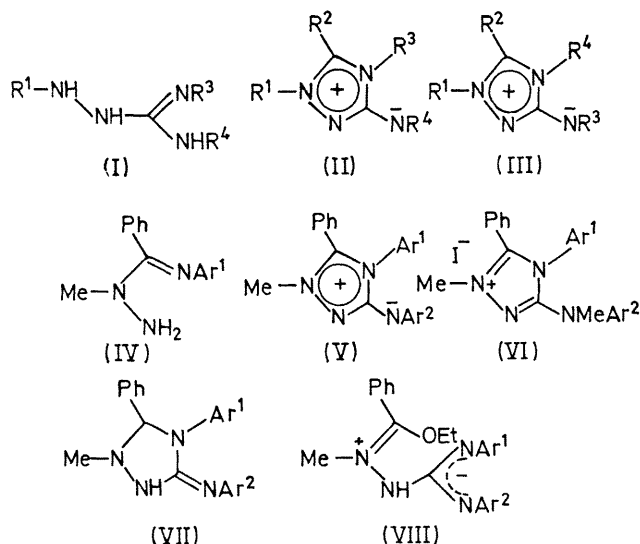
Synthesis and Isomerisation of Meso-ionic Anhydro-2-arylamino-1,3,4-triazolium Hydroxides

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Summary A synthetic route for the specific synthesis of the isomeric meso-ionic anhydro-2-arylamino-1,3,4-triazolium hydroxides (II) and (III) is described.

ANHYDROACYLATION of aminoguanidines (I) yielding meso-ionic 2-arylamino-1,3,4-triazoles (II) or (III) is an established reaction,¹ but for the case (I; $R^3 \neq R^4$) it has not been shown if the product is a single isomer [*e.g.* (II)] or a mixture (II + III). We now report upon the specific synthesis of isomers (II) and (III) and their interconversion.



In formulae (IV)–(VIII): (a) $Ar^1 = p\text{-ClC}_6\text{H}_4$, $Ar^2 = \text{Ph}$; (b) $Ar^1 = \text{Ph}$, $Ar^2 = p\text{-ClC}_6\text{H}_4$; (c) $Ar^1 = p\text{-MeC}_6\text{H}_4$, $Ar^2 = \text{Ph}$; (d) $Ar^1 = \text{Ph}$, $Ar^2 = p\text{-MeC}_6\text{H}_4$; (e) $Ar^1 = p\text{-MeOC}_6\text{H}_4$, $Ar^2 = \text{Ph}$.

The possibility of extending our use of isocyanide dichlorides for the synthesis of meso-ionic compounds² encouraged the examination of the reaction of isocyanide dichlorides with *N*-aminoamidines (IV). These compounds (IV), which are prepared from imido-chlorides ($\text{Ph-CCl}=\text{NAr}^1$) and *N*-methylhydrazine, reacted with isocyanide dichlorides in boiling toluene giving the intermediate 2-arylamino-1,3,4-triazolium chlorides. These intermediates were transformed into the yellow crystalline meso-ionic products (V) by treatment with aqueous ammonium hydroxide. This route was adopted for the specific synthesis of the following pairs of isomers: (Va) m.p. 231° decomp. and (Vb) m.p. 224°; (Vc) m.p. 229° decomp. and (Vd) m.p. 220°. The compound (Ve) m.p. 230° decomp. as well as several other compounds (V; $Ar^1 = Ar^2$) were also prepared. The characterisation of these compounds is exemplified by the isomers (Va) and (Vb). Anhydro-1-*p*-chlorophenyl-4-methyl-5-phenyl-2-phenylamino-1,3,4-triazolium hydroxide (Va) had properties [λ_{max} (EtOH) 247 nm (ϵ 22,400); ν_{max} (CHCl_3) 1550 cm^{-1} ; n.m.r. (CDCl_3) τ 6.30 (NMe); and a dipole moment [$\mu(\text{C}_6\text{H}_6)$ 8.2 D] which may be compared with the corresponding properties of anhydro-2-*p*-chlorophenylamino-1,5-diphenyl-4-methyl-1,3,4-triazolium hydroxide (Vb) [λ_{max} (EtOH) 256 nm (ϵ 29,100) and 288 nm (ϵ 14,900); ν_{max} (CHCl_3) 1550 cm^{-1} ; n.m.r. (CDCl_3) τ 6.25; and $\mu(\text{C}_6\text{H}_6)$ 9.9 D].

Significant differences between the mass spectra of the isomers (Va) and (Vb) were noted [(Va) $\rightarrow \text{Ph-C}\equiv\text{N}^+-\text{C}_6\text{H}_4\text{Cl}$ (Vb) $\rightarrow \text{Ph-C}\equiv\text{N-Ph}$]. These isomers (Va) and (Vb) yielded isomeric products with methyl iodide [(Va) \rightarrow (VIa), (Vb) \rightarrow (VIb)] and with lithium aluminium hydride [(Va) \rightarrow (VIIa), (Vb) \rightarrow (VIIb)]. The relative thermodynamic stability of the isomers (Va) and (Vb) is indicated by their equilibration in boiling ethanol: the meso-ionic compound (Va) is completely transformed into the isomer (Vb) whereas (Vb) is recovered unchanged. Under similar

conditions (Vc) and (Vd) each gave an equilibrium mixture a betaine intermediate (VIII)^{2,3} or the equivalent cation. [(Vc): (Vd) *ca.* 1 : 1] whereas (Ve) was recovered unchanged. The interconversion (II) \rightleftharpoons (III) presumably involved either

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² W. D. Ollis and C. A. Ramsden, *Chem. Comm.* 1971, 1222, 1223.

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