Synthesis of Meso-ionic Anhydro-2-arylamino-1,3,4-oxadiazolium Hydroxides

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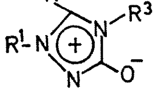
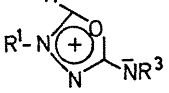
Summary The synthesis and characterisation of anhydro-2-arylamino-1,3,4-oxadiazolium hydroxides (II), a new class of meso-ionic compounds, is described.

MESO-IONIC compounds (I) are well-known,[1] but the synthesis of their isomers (II) has not been previously described. The synthesis[2] of meso-ionic anhydro-2-arylamino-1,3,4-thiadiazolium hydroxides (III) encouraged the examination of the reaction between *N*-benzoyl-*N*-methylhydrazine ($\mathrm{Ph{-}CO{-}NMe{-}NH_2}$) and arylisocyanide dichlorides ($\mathrm{ArN{=}CCl_2}$). These reagents in boiling benzene yielded the 1,3,4-oxadiazolium chlorides (IVa, b, and c), but cation deprotonation by various bases was initially unsuccessful owing to the instability of the meso-ionic products. However, the 1,3,4-oxadiazolium chlorides (IVa, b, and c) in dichloromethane with ethereal diazomethane did yield the yellow meso-ionic 1,3,4-oxadiazoles [(Va) m.p. 123°, (Vb) m.p. 136°, and (Vc) m.p. 130°] which were stable in the crystalline state.

Anhydro-4-methyl-5-phenyl-2-phenylamino-1,3,4-oxadiazolium hydroxide (Va) had properties [λ_{max} ($\mathrm{CH_2Cl_2}$) 250 nm (ϵ 22,800) and 324 nm (ϵ 6300); ν_{max} ($\mathrm{CH_2Cl_2}$) 1640 cm^{-1}; n.m.r. ($\mathrm{CDCl_3}$) τ 6·06 (NMe); mass spectrum $M^{+\cdot}$ 251; $\mathrm{Ph{-}C{\equiv}\overset{+}{O}}$ *m/e* 105; and dipole moment $\mu(\mathrm{C_6H_6})$ 7·6 D] in accord with its meso-ionic formulation; its reaction in methylene chloride solution with hydrogen chloride regenerated the 1,3,4-oxadiazolium chloride (IVa).


(I)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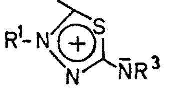
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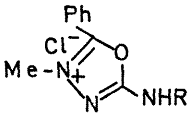
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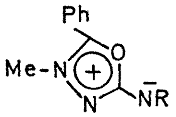
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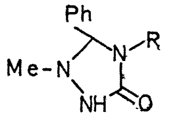
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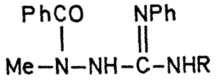
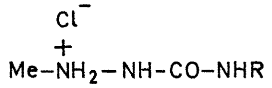


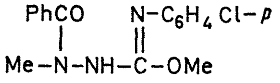
$$\mathrm{Me{-}\overset{\displaystyle PhCO}{\overset{|}{N}}{-}NH{-}\overset{\displaystyle NPh}{\overset{\|}{C}}{-}NHR}$$

(VII)



$$\mathrm{Me{-}\overset{\overset{\displaystyle Cl^{-}}{+}}{N}H_2{-}NH{-}CO{-}NHR}$$

(VIII)



$$\mathrm{Me{-}\overset{\displaystyle PhCO}{\overset{|}{N}}{-}NH{-}\overset{\displaystyle N{-}C_6H_4Cl{-}\mathit{p}}{\overset{\|}{C}}{-}OMe}$$

(IX)

In formulae (IV)—(VIII): (a) R = Ph; (b) R = p-$\mathrm{MeC_6H_4}$; (c) R = p-$\mathrm{ClC_6H_4}$

N-Benzoyl-*N*-methylhydrazine and phenyl isocyanate gave a semicarbazide (Ph–CO–NMe–NH–CO–NH–Ph) which, with sodium ethoxide in boiling ethanol, gave the stable meso-ionic compound (I; $R^1 = Me$; $R^2 = R^3 = Ph$) m.p. 242°. However, in spite of the stability of this compound, all attempts to achieve its formation from its isomer (Va) failed. Lithium aluminium hydride reduction of the compound (I; $R^1 = Me$; $R^2 = R^3 = Ph$) gave the 1,3,4-triazolidin-2-one (VI), but similar reduction of the compounds (Va, b, and c) was unrewarding. The meso-ionic compound (Va) reacted with aniline in boiling dichloromethane giving the aminoguanidine (VII). The reaction of the 1,3,4-oxadiazolium chlorides (IV) in methanol solution at room temperature shows a remarkable difference: compounds (IVa) and (IVb) give the hydrochlorides (VIIIa) and (VIIIb) directly, whereas the compound (IVc) gives the product (IX). The isomeric meso-ionic systems (I) and (II) are easily distinguished by mass spectrometry [(I) → $R^2\text{–}C{\equiv}\overset{+}{N}\text{–}R^3$, (II) → $R^2\text{–}C{\equiv}\overset{+}{O}$].

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[1] W. Baker and W. D. Ollis, *Quart. Rev.*, 1957, **11**, 15; M. Ohta and H. Kato, in 'Nonbenzenoid Aromatics,' ed. J. P. Snyder, Academic Press, New York, 1969, pp. 117—248.

[2] W. D. Ollis and C. A. Ramsden, preceding communication.