Synthesis of Meso-ionic Anhydro-2-arylamino-1,3,4-thiadiazolium Hydroxides and the Rearrangement of Meso-ionic 1,3,4-Thiadiazoles to Meso-ionic 1,3,4-Triazoles

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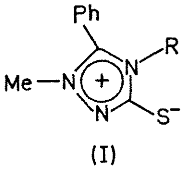
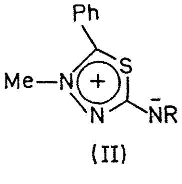
Summary The synthesis of anhydro-2-arylamino-1,3,4-thiadiazolium hydroxides (II), a new class of meso-ionic heterocycle, and two routes for their conversion into anhydro-2-mercapto-1,3,4-triazolium hydroxides (I) are described.

COMPOUNDS of the meso-ionic type (I) have been known for many years[1], but only recently has the possibility[2] of their representation by the alternative formulation (II) been firmly excluded.[3] We now report upon a specific synthetic route leading to the new class of meso-ionic compounds (II) and two quite different processes for effecting the isomerisation (II) → (I).

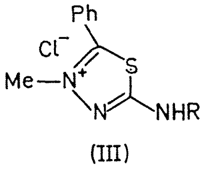
Isocyanide dichlorides[4] ($R\text{–}N{=}CCl_2$) and *N*-methyl-*N*-thiobenzoylhydrazine[5,6] ($Ph\text{–}CS\text{–}NMe\text{–}NH_2$) in boiling chloroform yielded the yellow crystalline thiadiazolium chlorides [(IIIa) m.p. 195°, (IIIb) m.p. 213°, and (IIIc) m.p. 220°] which, by treatment of their chloroform solution with anhydrous ammonia, yielded the meso-ionic compounds (IIa, b, and c) which were obtained as deep red oils; their characterisation is represented by the properties and reactions of anhydro-4-methyl-5-phenyl-2-phenylamino-1,3,4-thiadiazolium hydroxide. Its properties [λ_{max} (EtOH) 254 nm (ϵ 11,300), 408 nm (ϵ 4100); ν_{max} ($CHCl_3$) 1570 cm^{-1}; n.m.r. ($CDCl_3$) τ 6·14 (NMe); mass spectrum $M^{+\cdot}$ 267; $Ph\text{–}\overset{+}{C}{\equiv}S$, *m/e* 121; $Me\text{–}\overset{+}{N}{\equiv}CPh$, *m/e* 118; and dipole moment $\mu(C_6H_6)$ 6·7 D] are consistent with the formulation (IIa). Its treatment in chloroform solution with hydrogen chloride regenerates the thiadiazolium chloride (IIIa); dilute nitric acid gave the corresponding nitrate (m.p 225°) and methyl iodide in benzene solution gave the iodide [(IV) m.p. 115°].



(I)



(II)

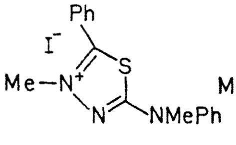


(III)

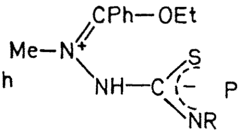
(a) R = Ph; (b) R = p-MeC_6H_4; (c) R = p-ClC_6H_4; (d) R = Me

The isolation of the meso-ionic compound (IId) was not achieved, although it was probably formed when the thiadiazolium chloride (IIId) was treated with ammonia; the product actually isolated was the meso-ionic isomer

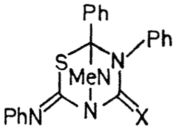
(Id). Similarly, the new meso-ionic heterocycles (IIa, b, and c) were totally transformed into their isomers (Ia, b, and c) by heating in ethanol. This rearrangement (II) → (I) presumably involves a betaine intermediate (V) similar to that already proposed[6] for the analogous conversion of meso-ionic 1,3,4-oxadiazoles into 1,3,4-thiadiazoles.



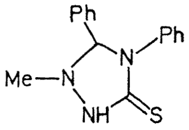
(IV)



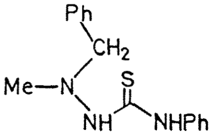
(V)



(VIa) X = S
(VIb) X = O



(VII)



(VIII)

A novel method for effecting the isomerisation (II) → (I) is illustrated by the reaction between the 1,3,4-thiadiazol-2-imine (IIa) and phenylisothiocyanate in benzene solution at room temperature. This yielded the isomeric meso-ionic 1,3,4-triazole (Ia). The presumption that this isomerisation (IIa) → (Ia) involves the 1,3-dipolar cyclo-adduct (VIa) has precedent[7] and is supported by the isolation of the 1,3-dipolar cyclo-adduct (VIb) when the compound (IIa) is treated with phenylisocyanate.

The distinction between the meso-ionic systems (I) and (II) by mass spectrometry is straightforward. Both systems (I) and (II) show a molecular ion and a common fragment ion, $\text{Me}\overset{+}{\text{N}}{\equiv}\text{CPh}$, but they are distinguished by the difference: (I) → $\text{Ph-C}{\equiv}\overset{+}{\text{N}}\text{R}$ and (II) → $\text{Ph-C}{\equiv}\overset{+}{\text{S}}$. A chemical differentiation is provided by lithium aluminium hydride reduction: (Ia) → (VII) and (IIa) → (VIII).

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