The Synthesis of Meso-ionic Anhydro-2-hydroxy-1,3,4-thiadiazolium Hydroxides and the Rearrangement of Meso-ionic 1,3,4-Oxadiazoles to Meso-ionic 1,3,4-Thiadiazoles

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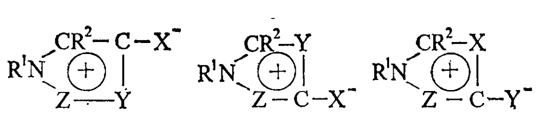
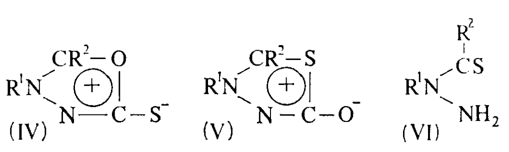
WHEN the term meso-ionic was first proposed,[1] a number of structural types belonging to this general class[2] of heterocycles was recognised and the possible existence of new types was predicted.[1,3] At first, representative types included, for example, the sydnones (Ia),[1,2,4] the 1,3,4-thiadiazoles (IIa),[5] and the 1,3,4-triazoles (IIb).[6] Recently several interesting new additions to the meso-ionic class have been made and these include the isosydnones (IIc),[7] the meso-ionic oxazolones (Ib)[8] and their sulphur-containing relatives (Ic and Id),[8] and some meso-ionic 1,3,4-triazoles (IId and IIe).[9]



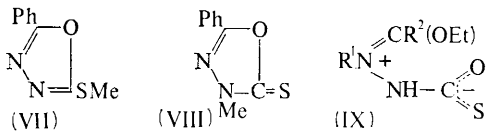
(I) (II) (III)

	X	Y	Z		X	Y	Z
(Ia)	O	O	N	(IIa)	S	S	N
(Ib)	O	O	CR^3	(IIb)	NR^3	NR^4	N
(Ic)	S	S	CR^3	(IIc)	O	O	N
(Id)	O	S	CR^3	(IId)	O	NR^3	N
				(IIe)	S	NR^3	N

Although the existence of isomers of the general types (II) and (III) has been recognised in principle,[1] as far as we are aware no example of this isomerism has been described and neither is information available regarding the possible interconversions (II → III) or (III → II). We now report on examples of the isomerism (IV and V) and the rearrangement (IV → V).



(IVa) (Va) (VIa) R^1 = Me, R^2 = Ph
(Vb) (VIb) R^1 = R^2 = Ph



Treatment of the isosydnone (IIc; R^1 = Me; R^2 = Ph)[7] with hydrogen sulphide in pyridine–chloroform solution at room temperature yielded *N*-methyl-*N*-thiobenzoylhydrazine (VIa),[10] the hydrochloride of which by heating with phosgene in ethyl acetate solution gave anhydro-2-hydroxy-4-methyl-5-phenyl-1,3,4-thiadiazolium hydroxide (Va) [m.p. 168—170°; ν_{max} (CHCl$_3$) 1652 cm.$^{-1}$; λ_{max} (EtOH) 232 mμ (ϵ 7450), 317 mμ (ϵ 6900); n.m.r. (CDCl$_3$) τ 2·42 singlet (C$_6$$H_5$), 6·10 singlet (C$H_3$)]. 4,5-Diphenylisosydnone (IIc; R^1 = R^2 = Ph) similarly gave *N*-phenyl-*N*-thiobenzoylhydrazine (VIb) which was transformed into anhydro-2-hydroxy-4, 5-diphenyl-1,3,4,-thiadiazolium hydroxide (Vb) [yellow prisms, m.p. 176—178°; ν_{max} ($CHCl_3$) 1653 cm.$^{-1}$; λ_{max} (EtOH) 234 mμ (ε 13,300), 335 mμ (ε 6800); n.m.r. ($CDCl_3$) τ 2·45—2·90 multiplet]. These two substances (Va and Vb) represent a new type of meso-ionic heterocycle and the study of their chemistry is in progress. In their general reactivity towards nucleophiles, these compounds (V) resemble the comparatively unreactive 1,3,4-thiadiazoles (IIa) rather than the isosydnones (IIc) which react easily with alcohols, water, and amines.

The compound (Va; m.p. 168—170°) is clearly different from its isomer (IVa; m.p. 227—229°) prepared by Sandström and Wennerbeck[11] who showed that reaction of the 1,3,4-oxadiazole (VII) with methyl iodide gave a mixture of two methiodides which yielded the 1,3,4-oxadiazole (VIII) and the meso-ionic compound (IVa) by heating with pyridine. These observations have been confirmed in all respects. Furthermore, although the meso-ionic 1,3,4-oxadiazole (IVa) is quite stable in boiling solvents such as pyridine, benzene, tetrahydrofuran, acetone, or acetic acid, it is quantitatively transformed into the isomeric meso-ionic compound (Va) either in boiling ethanol solution (48 hr.) or in boiling benzene-ethanethiol solution (48 hr.); the same transformation takes place more slowly in boiling t-butyl alcohol. Thus, the existence and interconversion of the isomeric meso-ionic compounds (IVa and Va) is established. The rearrangement (IVa→Va) which takes place in boiling ethanol could well involve the betaine-intermediate (IX).

The constitutions of the isomers (IVa) and (Va) are fully supported by their mass spectra. Thus the compound (IVa) and the corresponding isosydnone (IIc; R^1 = Me, R^2 = Ph) both showed the fragment ions (*m/e* 105; $Ph{\cdot}C{\equiv}O^+$) and (*m/e* 77; Ph^+) with the appropriate metastable peaks for the transformations: $M^+ \rightarrow Ph{\cdot}C{\equiv}O^+ \rightarrow Ph^+$. In contrast, the compound (Va) gave fragment ions (*m/e* 121; $Ph{\cdot}C{\equiv}S^+$) and (*m/e* 77, Ph^+) and metastable peaks for transformations: $M^+ \rightarrow Ph{\cdot}C{\equiv}S^+ \rightarrow Ph^+$.

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