Synthesis of Three New Meso-ionic Heterocyclic Systems

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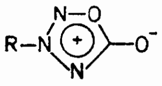
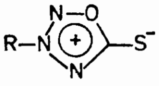
Summary The synthesis and characterisation of meso-ionic 1,2,3,4-oxatriazolium-5-thiolates (II), 1,2,3,4-thiatriazolium-5-olates (III), and 1,2,3,4-thiatriazolium-5-thiolates (IV), three new classes of meso-ionic heterocycle, are described; the 1,2,3,4-oxatriazolium-5-thiolates (II) rearrange to the 1,2,3,4-thiatriazolium-5-olates (III) in ethanol–ammonium hydroxide.

THE meso-ionic[1] 1,2,3,4-oxatriazolium-5-olates (I) are well-known,[2] but sulphur-containing analogues have not been described. We now report upon the synthesis and properties of the three new meso-ionic classes: 1,2,3,4-oxatriazolium-5-thiolates (II), 1,2,3,4-thiatriazolium-5-olates (III), and 1,2,3,4-thiatriazolium-5-thiolates (IV).



(I)



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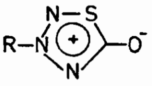

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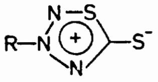

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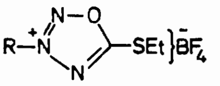
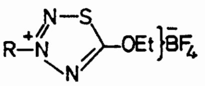


(V)



(VI)

Arylhydrazines and carbon disulphide in ethanol yield arylhydrazinium dithiocarbamate salts, $[Ar{\cdot}NH{\cdot}NH_3{}^+]$ $[{}^-S{\cdot}CS{\cdot}NH{\cdot}NHAr]$.[3] Nitrosation (sodium nitrite–aqueous hydrochloric acid) at 0° of a suspension in chloroform of these salts yielded yellow crystalline 1,2,3,4-oxatriazolium-5-thiolates (II; R = Ph, p-Me·C_6H_4, p-Cl·C_6H_4, p-MeO·C_6H_4, or p-EtO·C_6H_4). These novel meso-ionic heterocycles (II) are isomerised by warming with ethanol–ammonium hydroxide yielding colourless crystalline 1,2,3,4-thiatriazolium-5-olates (III).

Meerwein alkylation (triethyloxonium tetrafluoroborate[4] in methylene chloride) of the meso-ionic heterocycles (II) and (III) gave the corresponding salts (V) and (VI). The salts (V) did not react satisfactorily with nucleophiles, whereas the salts (VI) gave interesting examples of new classes of meso-ionic heterocycles by reaction with sodium sulphide, amines, and malononitrile. These sequences show how Meerwein alkylation followed by reaction with nucleophiles may be used to synthesise new classes of meso-ionic compounds.

The 5-ethoxy-1,2,3,4-thiatriazolium tetrafluoroborate (VI) with sodium sulphide in aqueous dimethylformamide (room temperature, 2 h) gave the orange crystalline 3-aryl-1,2,3,4-thiatriazolium-5-thiolates (IV; R = Ph, p-Me·C_6H_4, or p-Cl·C_6H_4).

The existence of the pairs of meso-ionic isomers (II) and (III) is of particular interest[5,6] and although the mechanism of the transformation (II → III) by ethanolic ammonium hydroxide has not been established, clearly, in the cases studied, the isomers (III) with endocyclic-sulphur and exocyclic-oxygen atoms are thermodynamically preferred. The absence of absorption (ν_{NCO} *ca.* 2260 cm^{-1}; ν_{NCO} *ca.* 2260 cm^{-1}) in the i.r. spectra of the compounds (II) and (III) excludes alternative valence tautomeric structures. Furthermore, their u.v., i.r., and n.m.r. spectra and their dipole moments fully support their meso-ionic formulation.[1]

The isomers (II; R = Ph; μ = 6·83D) and (III; R = Ph; μ = 4·39D) show interesting differences in their dipole moments in benzene solution. Comparison of their mass spectra is highly informative and clearly distinguishes between the isomers (II) and (III) which show in addition to parent peaks ($M^{\cdot+}$) the fragment ions ($II \rightarrow M^{\cdot+} - NO^{\cdot}$) and ($III \rightarrow M^{\cdot+} - NS^{\cdot}$).

Acid hydrolysis of (II; R = Ph) gives phenol, whereas the isomer (III; R = Ph) is stable; alkaline hydrolysis (boiling aqueous sodium hydroxide) of both isomers yields phenyl azide.

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