Meso-ionic 1-Amino-1,3,4-triazolium-2-thiolates

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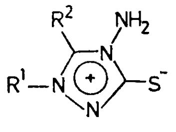
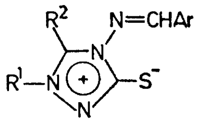
Summary Complementary synthetic routes to meso-ionic 1-amino-1,3,4-triazolium-2-thiolates (I) are established and earlier work on the nitrosation of the *N*-amino-compound (Ia) is corrected.

The 1-amino-1,3,4-triazolium-2-thiolate (Ia) has recently been synthesised[1] by Lazaris, Shmuilovich, and Egorochkin and characterised[1] as the benzylidene derivative (IIa). These two compounds have also been obtained in our investigation[2] of meso-ionic 1,3,4-thiadiazolium-2-benzylidenehydrazinides. However, the claim[1] that nitrosation of the *N*-amino-derivative (Ia) yields 4,5-diphenyl-(3*H*)-1,3,4-triazole-2-thione (III) or a tautomer is not correct. The nitrosation product, m.p. 178° (lit.[1] 182—183°) is, in fact, the known disulphide (IV) previously prepared[3] (lit.[3] 174°) by oxidation of 4,5-diphenyl-(3*H*)-1,3,4-triazole-2-thione (III).[4]

The disulphide (IV) undergoes an unexpected transformation by Raney nickel desulphurisation yielding *N'*-cyano-*N*-phenylbenzamidine (V; m.p. 234°) which was similarly

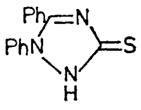


(I)

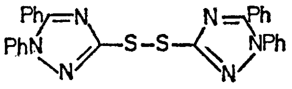


(II)

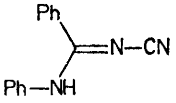
(a) $R^1 = R^2 = Ph$; (b) $R^1 = R^2 = Me$; (c) $R^1 = Me, R^2 = Ph$; (d) $R^1 = Ph, R^2 = Me$; (e) $R^1 = H, R^2 = Ph$



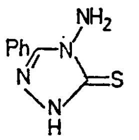
(III)



(IV)



(V)



(VI)

formed from 4,5-diphenyl-(3*H*)-1,3,4-triazole-2-thione (III). The constitution (V or its tautomer) was confirmed by its direct synthesis from *N*-phenylbenzimidoyl chloride and cyanamide in boiling benzene.

The meso-ionic compounds (Ia—d) were synthesised by the sequence (1).

$$R^2\text{-CO-NR}^1\text{-NH}_2 \xrightarrow[\text{NEt}_3]{\text{CS}_2} R^2\text{-CO-NR}^1\text{-NH-CS}_2^-\} + \text{NEt}_3\text{H}$$
$$\xrightarrow{\text{ClCH}_2\text{CO}_2\text{Na}} R^2\text{-CO-NR}^1\text{-NH-CS-S-CH}_2\text{CO}_2\text{Na}$$
$$\xrightarrow{\text{N}_2\text{H}_4} (\text{Ia—d}) \qquad (1)$$

The possibility of preparing a compound (Ie) by a corresponding route from *N*-benzoylhydrazine (VII; $R^1 = H$, $R^2 = Ph$) was examined: the product (m.p. 204°) is identical with the compound (lit.[5] 202—204°) prepared by a different route.[5] Comparison of the spectroscopic properties of the compound (m.p. 204°) with the meso-ionic compounds (Ia—d) clearly indicates that it has the tautomeric structure (VI). This preference for the covalent structure (VI) rather than the meso-ionic tautomer (Ie) may be compared with the corresponding equilibrium between Δ^2-oxazolin-5-ones and their tautomeric meso-ionic equivalents, 1,3-oxazolium-5-olates.[6]

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