Synthesis of Four New Meso-ionic Heterocyclic Systems

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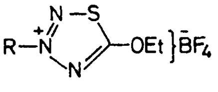
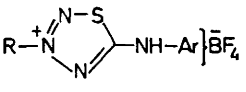
Summary The synthesis of derivatives of four new meso-ionic heterocyclic systems (III), (IV), (IX), and (X) has been achieved; the possible interconversion of the isomers (III) and (IV) has been examined.

5-Ethoxy-1,2,3,4-thiatriazolium tetrafluoroborates (Ia—f)[1] with aromatic amines in boiling benzene yield the yellow crystalline 5-arylamino-1,2,3,4-thiatriazolium tetrafluoroborates (IIa—f). These salts (IIa—f) are deprotonated with warm ethanolic aqueous sodium hydroxide yielding the red crystalline meso-ionic 1,2,3,4-thiatriazolium-5-aminides (IIIa—f). The yellow crystalline meso-ionic isomers (IVa, d—g) have been prepared by the following sequence. Meerwein alkylation of the known[2] meso-ionic 1,2,3,4-tetrazolium-5-olates (Va, d—g) gave the salts (VIa, d—g) which with sodium sulphide in hot dimethylformamide solution yields the meso-ionic 1,2,3,4-tetrazolium-5-thiolates (IVa, d—g).

The existence of pairs of isomers of two new classes of meso-ionic heterocycles (III) and (IV) is of interest and their meso-ionic formulation is fully supported by their u.v., i.r., and n.m.r. spectra. Distinctive differences exist between the dipole moments of the isomers (IIIa; μ = 3·71D) and (IVa; μ = 6·52D). Informative differences exist in their mass spectral fragmentation: (IIIa; $M^{\cdot +} \rightarrow$ Ph$\overset{+}{\text{N}}$=N=S) and (IVa; $M^{\cdot +} \rightarrow$ Ph$-\overset{+}{\text{N}}\equiv$N).


(I)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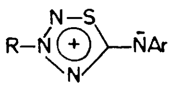
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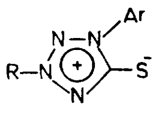
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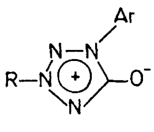
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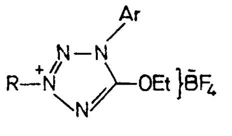
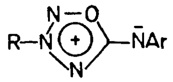
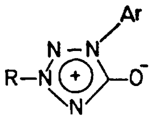
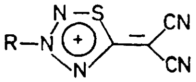

(VI)

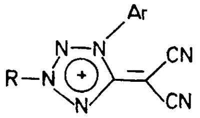
(a) R = Ar = Ph; (b) R = Ph, Ar = p-Me·C_6H_4; (c) R = p-Me·C_6H_4, Ar = Ph; (d) R = Ar = p-Me·C_6H_4; (e) R = Ph, Ar = p-Cl·C_6H_4; (f) R = p-Cl·C_6H_4, Ar = Ph; (g) R = Ar = p-Cl·C_6H_4.


(VII)


(VIII)

The base-catalysed rearrangement (VII → VIII) is well established,[3] but all attempts to effect the transformation (III → IV) or (IV → III) have been unsuccessful.


(IX)


(X)

(a) R = Ar = Ph; (b) R = Ar = p-Me·C_6H_4; (c) R = Ar = p-Cl·C_6H_4.

An interesting recent development in the chemistry of meso-ionic heterocycles was the discovery that the exocylic carbanionoid group could be —$\bar{C}(CN)_2$.[4] In this connection, two new classes of meso-ionic heterocycles (IXa—c) and (Xa,b) have been synthesised by reaction of the salts (I) and (VI) with malononitrile and triethylamine in acetonitrile. These biscyanomethylide derivatives (IX) and (X) are yellow to orange in colour and they have large dipole moments (IXa; μ = 8·84D) and (Xa; μ = 9·54D).

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[1] R. N. Hanley, W. D. Ollis, and C. A. Ramsden, preceding communication.

[2] H. von Pechmann, *Ber.*, 1896, **29**, 2161; W. V. Farrar, *J. Chem. Soc.*, 1964, 906.

[3] M. Busch and J. Becker, *Ber.*, 1896, **29**, 1686; M. Busch and W. Schmidt, *Ber.*, 1929, **62**, 1449; C. Christopherson and S. Treppendahl, *Acta Chem. Scand.*, 1971, **25**, 625.

[4] R. Grashey and M. Baumann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 133.