Meso-ionic 1,3,4-Thiadiazoles: Reaction with Dialkyl Azodicarboxylates and Formation of a New Meso-ionic System

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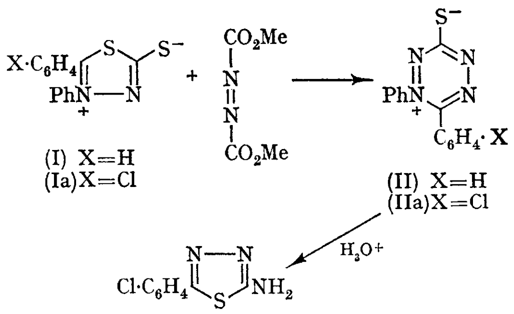
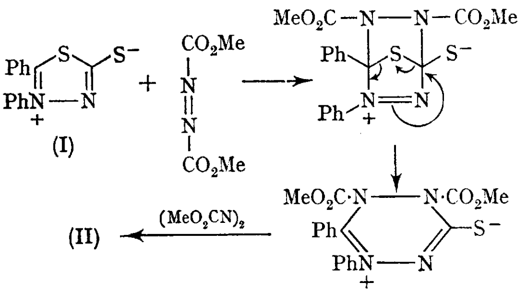
Sydnones have been shown to undergo 1,3-dipolar type cycloaddition.[1] The less studied meso-ionic compounds, 1,3,4-thiadiazoles (*anhydro*-4,5-diaryl-1-thia-2-thio-3,4-diazolium thiols)[2] might also undergo 1,3-dipolar cycloaddition with accompanying loss of carbon disulphide to yield five-membered heterocyclic derivatives. In contrast to unpromising results experienced with olefinic and acetylenic dipolarophiles, the reaction of 4,5-diaryl meso-ionic 1,3,4-thiadiazoles with dialkyl azodicarboxylates affords high yields of adducts. The adducts (II, IIa) are members of a new class of six-membered meso-ionic compounds, and the proposed pathway for their formation resembles formally a Diels–Alder reaction rather than a 1,3-dipolar cycloaddition.

Typically, reaction of meso-ionic 4,5-diphenyl-1-thia-2-thio-3,4-diazolium thiol (I) with a two-fold molar excess of dimethyl azodicarboxylate in benzene under reflux for 12 hr. yielded 62% of adduct (II), with a 98% yield of sulphur and about 96% of dimethyl hydrazodicarboxylate.



Compound (II), m.p. 175—176° (sub.) had λ_{max} 265 mμ (log ε 4·03), 367 mμ (log ε 4·18). The infrared spectrum showed no NH or CO absorption. The composition of (II) as $C_{14}H_{10}N_4S$ was confirmed by microanalysis and molecular weight (Rast). The mass spectrum of (II) offered strong support for the proposed structure.



Scheme

The parent molecular ion $(C_{14}H_{10}N_4S)^+$, *m/e* 266, 30% confirmed the molecular weight. The n.m.r. spectrum showed the aromatic protons as a singlet resonance when deuterochloroform was used as solvent; however, two sets of aromatic protons were observed with dimethyl sulphoxide as solvent. Meso-ionic compound (II) formed a methiodide derivative of m.p. 170—171°, λ_{max} 262 mμ (log ε 3·88), 275 mμ (log ε 3·87).

Reaction of anhydro-4-phenyl-5-*p*-chlorophenyl-1-thia-2-thio-3,4-diazolium thiol (Ia) with dimethyl azodicarboxylate produced adduct (IIa), m.p. 176—177°, λ_{max} 235 mμ (log ε 4·09), 370 mμ (log ε

4·61. Catalytic hydrogenation yielded a dihydro-derivative, m.p. 205—207°, λ_{max} 232 mμ, (log ϵ 4·20); 308 mμ (log ϵ 4·14). Compound (IIa) formed a methiodide, m.p. 164—167°, λ_{max} 369 mμ (log ϵ 4·52). Compound (IIa) was hydrolyzed in 50% sulphuric acid to 2-amino-5-*p*-chlorophenyl-1,3,4-thiadiazole (III).[3]

Interaction of the anhydro 4,5-diaryl-1-thia-2-thio-3,4-diazolium thiols with dimethyl azodicarboxylate may proceed by the sequence shown in the Scheme.

In this mechanistic representation, the initial addition is represented by a Diels-Alder reaction, not as a 1,3-dipolar cycloaddition. Decarboalkoxylation of cyclic intermediates containing the $EtO_2C\cdot\overset{|}{N}-\overset{|}{N}\cdot CO_2Et$ group upon interaction with diethyl azodicarboxylate has already been observed by Professor R. Huisgen, who first suggested this mechanism to us.

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[1] R. Huisgen, H. Gotthardt, and R. Grashey, *Angew Chem.*, 1962, **74**, 29; R. Huisgen, R. Grashey, H. Gotthardt, and R. Schmidt, *ibid.*, p. 29; V. F. Vasil'eva, V. G. Yashubskii, and M. N. Shchukina, *Zhur. obshchei Khim.*, 1962, **32**, 1446 (*Chem. Abs.*, 1963, **58**, 9052); D. Ll. Hammick and D. J. Voaden, *J. Chem. Soc.*, 1961, 3303.

[2] These compounds were first reported in 1895 by Busch who suggested an unlikely bridged structure for them; M. Busch, *Chem. Ber.*, 1895, **28**, 2635. Schönberg thought that these bridged structures were in violation of Bredt's rule, and suggested charge separated resonance contributions, A. Schönberg, *J. Chem. Soc.*, 1938, 824. The mesoionic formulation has been suggested by W. Baker, W. D. Ollis, and V. D. Poole, *J. Chem. Soc.*, 1950, 1542.

[3] E. Hoarth, *J. Chem. Soc.*, 1949, 1163.