

A Revised Mechanism for the Cycloaddition of Mesoionic Dithioles with Heterocumulenes

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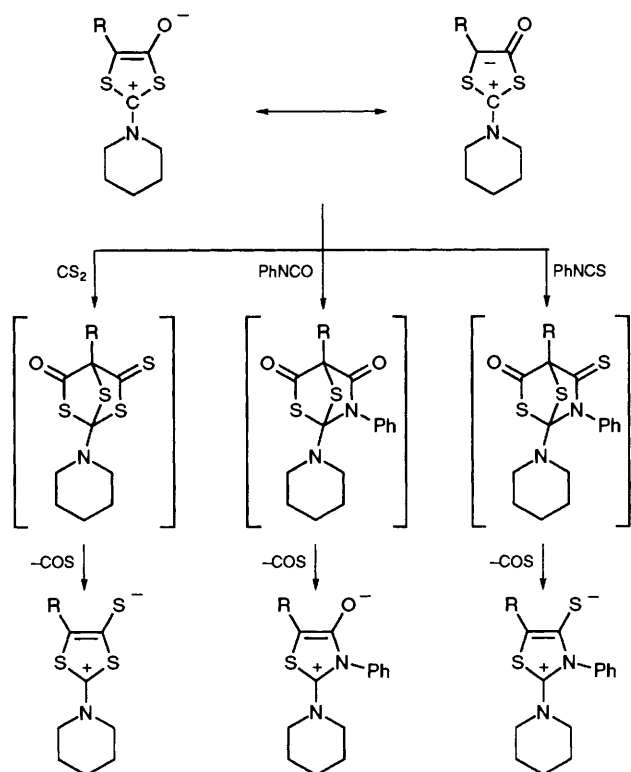
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The reaction of a mesoionic 1,3-dithiolium-4-olate with phenyl isocyanate is not a 1,3-dipolar cycloaddition as the primary cycloadduct is an azetidinedione which probably results from the addition of phenyl isocyanate with the opened ketene form of the mesoionic compound.

Mesoionic derivatives are of special interest in the field of 1,3-dipolar cycloadditions because they are quite stable 1,3-dipoles with a fixed geometry.¹⁻³ The reactions of heterocumulenes (CS₂, PhNCO, PhNCS) with mesoionic derivatives such as 1,3-oxazolium-5-olates (münchnones),⁴ or 1,3-dithiol-

ium-4-olates,⁵ have been studied in order to achieve the easy conversion of one mesoionic derivative into another. The reactions were thought to proceed through 1,3-dipolar cycloaddition-retrocycloaddition processes (Scheme 1).

However, as was the case with the more common dipolaro-



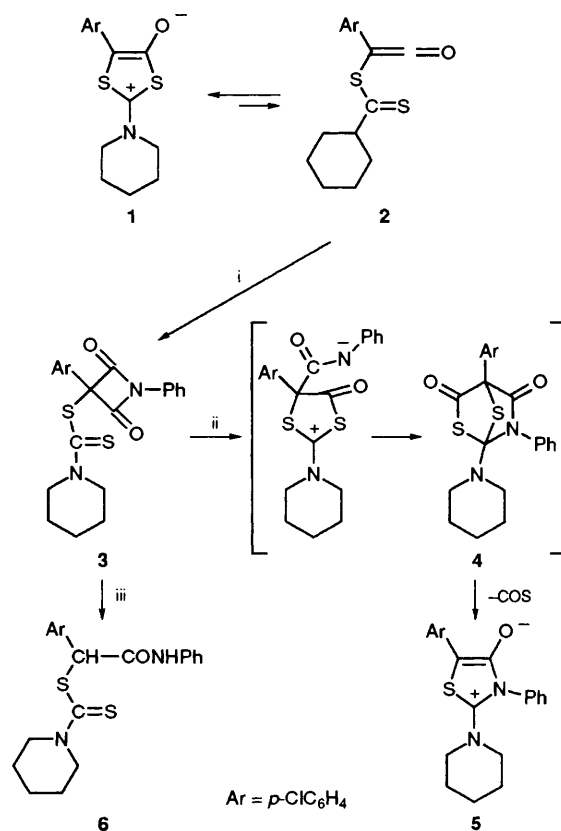
Scheme 1 1,3-Dipolar cycloaddition-retrocycloaddition mechanism which has been postulated for interconversions of mesoionic compounds

phile dimethyl acetylenedicarboxylate, the primary cycloadducts were postulated but never isolated. The mesoionic derivatives which are converted to other mesoionic derivatives through their reaction with CS_2 , PhNCO or PhNCS are also known to react with nucleophiles in their opened ketene form.^{1,6} Furthermore, while 1,3-dithiolium-4-olates reacted rapidly with the previous heterocumulenes, we observed no reaction with the quite good dipolarophiles dimethyl maleate and dimethyl fumarate.

We show in this communication that the reaction of the 1,3-dithiolium-4-olate **1** with phenyl isocyanate leads to an azetidinedione as the primary cycloadduct and, as a consequence, this reaction cannot be a 1,3-dipolar cycloaddition.

We have already shown that the 1,3-thiazolium-4-olate **5** is obtained from the reacting of the mesoionic 1,3-dithiolium-4-olate **1** and phenyl isocyanate in dry benzene under reflux for 1.5 h.⁵ By decreasing the reaction time (20 min) and after removal of solvent followed by the addition of dry diethyl ether to the oily residue, we have now been able to isolate the azetidinedione **3** [m.p. 150 °C decomp. (from EtOH); yield 93%] (Scheme 2).

Suitable single crystals could not be obtained for an X-ray crystallographic study, but the structure of the azetidinedione **3** is well established by other means: satisfactory microanalysis; IR (Nujol), three characteristic bands⁷ ($\nu_{\text{max}}/\text{cm}^{-1}$ 1865w, 1745s and 975w); ^1H NMR (CDCl_3) δ 1.70 (m, 6H), 3.95 (m, 4H) and 7.25–7.90 (m, 9H); ^{13}C NMR (CDCl_3) δ 189 (quint, 3J 4 Hz), 166 (s), 51 (tm, J 136 Hz), 52 (tm, J 138 Hz), 24 (tm, J 129 Hz), 25 (tm, J 133), 26 (tm, J 131 Hz) and 8 aryl carbons (119, 127, 128.6, 129.26, 129.3, 129.6, 134 and 136). It is also worth noting that when the interconversion of a mesoionic derivative into another is prevented by the structure of the adduct, similar four-membered rings have been isolated (for example during the reaction of 1,3-oxazolium-5-olate with substituted carbodiimides).¹ Furthermore, hydrolysis of **3** at room temperature with hydrochloric acid gave the expected amide **6** (via decarboxylation of a carbamic acid inter-



Scheme 2 Reagents and conditions: i, **1** (1 g), dry C_6H_6 (40 cm^3), PhNCO (2 cm^3), reflux 20 min; ii, **3** (0.2 g) dry C_6H_6 (15 cm^3), reflux, 1 h; iii, **3** (0.5 g), tetrahydrofuran (10 cm^3), aq. HCl (2 mol dm^{-3}), room temp., 2 h

mediate). The structure of **6** was deduced from its spectroscopic properties (IR, ^1H and ^{13}C NMR, high-resolution mass spectra).

The thermolysis of **3** in refluxing dry benzene for 1 h quantitatively gave the mesoionic 1,3-thiazolium-4-olate **5**⁵ with elimination of COS. COS was trapped with piperidine and characterized as the corresponding thiocarbamate salt, m.p. 114–115 °C (lit.⁸ 114–115 °C). It seems likely that the bicyclic compound **4** (also postulated as an intermediate in 1,3-dipolar mechanism, Scheme 1) is the intermediate losing COS during the thermolysis of **3**. Numerous attempts to isolate other four-membered ring intermediates in the interconversion of 1,3-dithiolium-4-olates or 1,3-dithiolium-4-thiolates failed. Nevertheless the isolation of **3** in good yield shows some cycloadditions of mesoionic derivatives in a different light.

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