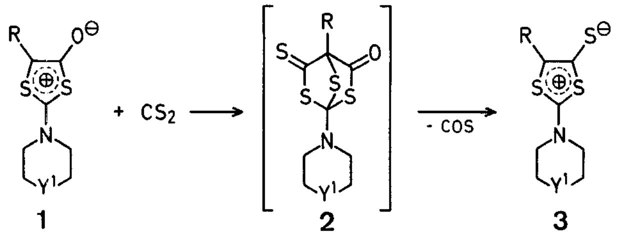
Interconversion of Mesoionic 1,3-Dithiolium-4-olates by Reaction with Carbon Disulfide, Phenyl Isocyanate, or Phenyl Isothiocyanate

A. Souizi, A. Robert*

Groupe de Chimie Structurale, Équipe Associée au C.N.R.S., F-35042
Rennes Cedex, France

The particular structure of mesoionic 1,3-dithiolium-4-olates gives these compounds interesting properties which have been investigated recently. Among these properties, the ability to undergo [1,3]-dipolar cycloadditions[1-7], head-to-head dimerisation[8], and the reactions with singlet or triplet oxygen[9] are worthy of notice. Mesoionic 4-thiolates without a nitrogen atom in the ring have not been prepared by a direct synthesis and the interconversion of a mesoionic-4-olate compound into a mesoionic 4-thiolate compound has only been observed with mesoionic oxazole systems[10,11].

We now describe the easy interconversion of mesoionic 1,3-dithiolium-4-olates **1** (prepared from 2,2-dicyanooxiranes[12]) into mesoionic 1,3-dithiolium-4-thiolates **3** by reaction with carbon disulfide, and the extension of this reaction to the interconversion of **1** into mesoionic 1,3-thiazolium-4-olates **4** or the mesoionic 1,3-thiazolium-4-thiolates **5** by reaction with phenyl isocyanate or phenyl isothiocyanate. The mesoionic 2-amino-1,3-dithiolium-4-olates **1** dissolved in anhydrous boiling benzene[13] reacted rapidly with carbon disulfide to give the corresponding mesoionic 2-amino-1,3-dithiolium-4-thiolates as orange solids which were characterized by microanalyses and I.R., U.V., ^{1}H-N.M.R., and mass spectrometry (Scheme **A** and Table 1). As previously observed for other mesoionic cycloadducts[14], the primary cycloadducts **2** may be too instable to be isolated. Carbon oxide sulfide was, however, trapped with piperidine and characterized.

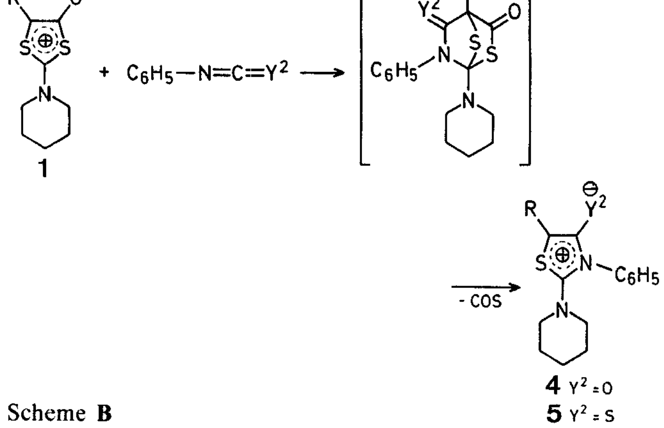


Scheme **A**

The reaction described in Scheme **A** was effective for all the mesoionic dithioles we have studied and yields were good in spite of the thermal instability of compounds **1**[15]. This reaction is of particular interest when R is an alkyl group as compounds **1** (R = alkyl) are too instable to be isolated, but their synthesis in the presence of carbon disulfide gives good yields in the corresponding mesoionic 1,3-dithiolium-4-thiolates **3** (R = alkyl) which are much more stable.

As the reaction of carbon disulfide with a mesoionic dithiole **1** allows the interconversion of a mesoionic compound into another mesoionic derivative, it was of interest to generalize this kind of reaction to other heterodipolarophiles. No reaction was observed in boiling benzene after half an hour when the reactant was diphenylcarbodiimide, while the only products isolated after a longer reaction time were the thermolysis products of **1**. No interconversion of **1** into mesoionic oxathioles was observed when carbon dioxide was the reactant.

However, the interconversion of the mesoionic dithioles **1** ($Y^1 = CH_2$) into the mesoionic 1,3-thiazolium-4-olates **4** or the mesoionic 1,3-thiazolium-4-thiolates **5** was achieved in good yields by reacting **1** with phenyl isocyanate or phenyl isothio-



Scheme **B**

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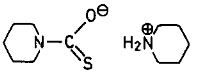
cyanate (Scheme **B**). These mesoionic compounds **4** and **5** were characterized by I.R., ^{1}H-N.M.R., and mass spectrometry (Table 2). The mesoionic thiazole **4** (R=*p*-Cl—C_6H_4) was also prepared according to a known reaction[17] and showed the same I.R. and ^{1}H-N.M.R. spectra as **4** obtained through the reaction of the dithiole **1** (R=*p*-Cl—C_6H_4, Y^1=CH_2) with phenyl isocyanate.

The mesoionic 2-amino-1,3-dithiolium-4-olates **1** were prepared from 2,2-dicyanooxiranes according to Ref.[12].

Mesoionic 2-Amino-1,3-dithiolium-4-thiolates 3 (R=aryl):

A mixture of the mesoionic 2-amino-1,3-dithiolium-4-olate **1** (1 g), carbon disulfide (5 ml) and dry benzene (40 ml) is heated under reflux for 20 min. The precipitated **3** is separated by filtration at room temperature and recrystallized from ethanol (Table 1).

Characterization of Carbon Oxide Sulfide:



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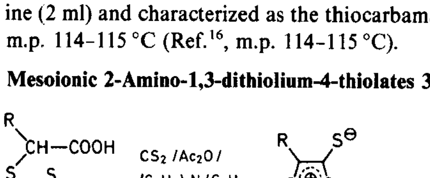
The gas formed during the preceding reaction is bubbled into piperidine (2 ml) and characterized as the thiocarbamate piperidinium salt **6**; m.p. 114-115 °C (Ref.[16], m.p. 114-115 °C).

Mesoionic 2-Amino-1,3-dithiolium-4-thiolates 3 (R=CH_3, C_2H_5):



7 R=CH_3, C_2H_5 **3** R=CH_3, C_2H_5

A mixture of the acid **7**[12] (0.5 g), dry benzene (10 ml), carbon disulfide (2 ml), acetic anhydride (2 ml), and triethylamine (1 ml) is stirred at room temperature for 20 min. The precipitated **3** is separated by filtration and recrystallized from ethanol (Table 1).

Mesoionic 1,3-Thiazolium-4-olates 4 and -4-thiolates 5:

The mesoionic 1,3-dithiolium-4-olate **1** (1 g) and phenyl isocyanate or isothiocyanate (2 ml) in dry benzene (40 ml) are heated under reflux for 1.5 h. The solvent is distilled and dry ether (15 ml) is added to the oily residue. The yellow precipitate of **4** (or **5**) is separated by filtration and recrystallized from ethanol (Table 2).

Compound **4** (R=*p*-Cl—C_6H_4, Y^1=CH_2) was also prepared according to Ref.[17].

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Table 1. Mesoionic 1,3-Dithiolium-3-thiolates **3**

Product No.	Y^1	R	Yield [%]	m.p. [°C]	Molecular formula[a]	M.S. *m/e* (M^+) (calc. for M^+)	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]	U.V. (C_2H_5OH) λ [nm] ($\varepsilon \cdot 10^{-3}$)
3a	CH_2	4-Cl—C_6H_4	95	266°	$C_{14}H_{14}ClNS_3$	326.9964 (326.9977)	1.6 (m, 6H); 3.6 (m, 4H); 7.7 (m, 4H)	277 (12.9); 337 (6.9); 357 (6.9)
3b	O	4-Cl—C_6H_4	86	258°	$C_{13}H_{12}ClNOS_3$	328.9763 (328.9769)	3.6 (m, 4H); 3.8 (m, 4H); 7.3 (m, 4H)	281 (12.5); 331 (7.4); 357 (7.0)
3c	CH_2	C_6H_5	90	251°	$C_{14}H_{15}NS_3$	293.0380 (293.0367)	1.7 (m, 6H); 3.5 (m, 4H); 7.75 (m, 4H)	278 (15.4); 332 (9.9); 357 (5.1)
3d	CH_2	4-H_3C—C_6H_4	91	260°	$C_{15}H_{17}NS_3$	307.0518 (307.0523)	1.7 (m, 6H); 2.59 (s, 3H); 3.5 (m, 4H); 7.6 (m, 4H)	281 (14.5); 327 (9.7); 352 (7.8)
3e	O	4-H_3C—C_6H_4	86	249°	$C_{14}H_{15}NOS_3$	309.0315 (309.0316)	2.33 (s, 3H); 3.5 (m, 4H); 3.7 (m, 4H); 7.6 (m, 4H)	280 (10.8); 326 (7.9); 346 (5.4)
3f	CH_2	CH_3	82	232°	$C_9H_{13}NS_3$	231.0210 (231.0210)	1.8 (m, 6H); 2.23 (s, 3H); 3.7 (m, 4H)	271 (14.1)
3g	CH_2	C_2H_5	91	225°	$C_{10}H_{15}NS_3$	245.0027 (245.0017)	1.20 (t, 3H); 1.8 (m, 6H); 2.74 (q, 2H); 3.7 (m, 4H)	272 (11.9)

[a] Satisfactory microanalyses obtained: C ±0.32, H ±0.14, N ±0.13, S ±0.19.

Table 2. Mesoionic Thiazoles **4** (Y^2=O) and **5** (Y^2=S)

Product No.	R	Yield [%]	m.p. [°C]	Molecular formula[a]	N.S. *m/e* (M^+) (calc. for M^+)	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]
4a[b]	4-Cl—C_6H_4	93	176°	$C_{20}H_{19}ClN_2OS$	370.0898 (370.0906)	1.5 (m, 6H); 3.1 (m, 4H); 7.5 (m, 9H)
5a	4-Cl—C_6H_4	92	266°	$C_{20}H_{19}ClN_2S_2$	386.0692 (386.0678)	1.5 (m, 6H); 3.1 (m, 4H); 7.3 (m, 9H)
5c	C_6H_5	87	236°	$C_{20}H_{20}N_2S_2$	352.1059 (352.1068)	1.5 (m, 6H); 3.1 (m, 4H); 7.75 (m, 10H)
5d	4-H_3C—C_6H_4	89	198°	$C_{21}H_{22}N_2S_2$	366.1214 (366.1224)	1.5 (m, 6H); 2.31 (s, 3H); 3.1 (m, 4H); 7.4 (m, 9H)

[a] Satisfactory microanalyses obtained: C ±0.34, H ±0.10, N ±0.30, S ±0.28.

[b] I.R. (nujol): ν=1632 cm^{-1} (C=O).

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