Synthesis of Novel Mesoionic Systems: 1,3-Oxathiolylium-4-thiolate and 1,3-Oxazolylium-4-thiolate. A Synthon allowing a New Approach to 1,4-Oxathiafulvene Derivatives

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By a convenient one pot reaction, dialkylamino(thiocarbonyloxy)phenylacetic acids (1) are converted into the novel 1,3-oxathiolylium-4-thiolates (6) or 1,3-oxazolylium-4-thiolate system (4) in high yields; the former mesoionic heteroarenes (6) readily combine with CH acidic compounds to give 1,4-oxathiafulvene derivatives (7) or (8).

Since the mesoionic heteroarenes possess considerable synthetic potential, the interest in the chemistry of these compounds has increased rapidly.¹ Recently, the synthesis of the first stable 1,3-oxathiolylium-4-olates,² a new class of mesoionic 6π heteroarenes, and their [3 + 2] cycloaddition reactions³ have been realized. Herein we report on the synthesis of the first 1,3-oxathiolylium-4-thiolates (6) and 1,3-oxazolylium-4-thiolates (4) as well as a new approach to 1,4-oxathiafulvene derivatives.

Thus, treatment of diethylamino(thiocarbonyloxy)phenylacetic acid^{\dagger} (1; R = NEt₂) with acetic anhydridetriethylamine in toluene in the presence of carbon disulphide

Table 1.	1,3-Oxathiolylium-4-thiolates	(6)	from	(1).
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(6)	R	% Yield	M.p. (<i>t</i> /°C) (decomp.)	U.v. (CHCl ₃) $\lambda_{max}/nm (\log \epsilon)$
a	NEt ₂	87	168	349 (4.21)
b	NMe_2	93	193.5194.5	349 (4.20)
с	Pyrrolidino	85	190-191	349 (4.27)
d	Piperidino	87	167—168	350 (4.16)
e	Morpholino	56	178179	349 (4.18)

[†] Synthesis in accordance with the procedure of H. Gotthardt *et al.* (ref. 4), m.p. 145–146 °C (decomp.), yield 75%.

at 50-60 °C produced yellow crystals of analytically pure 1,3-oxathiolylium-4-thiolate (6a) (Scheme 1, Table 1).‡

‡ All new compounds gave satisfactory microanalytical data. Spectroscopic data: (4): i.r. v(C-N) 1647 cm⁻¹; u.v. (CHCl₃) λ_{max} 345 nm (log ε 4.19); ¹H n.m.r. (CDCl₃) δ 8.33-8.17 (2H, m), 7.62-7.09 (8H, m), 3.27 (2NCH₂, q, J 7.0 Hz), and 1.10 (2Me, t, J 7.0 Hz); $^{13}C{^{1}H}$ n.m.r. (CDCl₃) δ 152.18 (C-2), 142.89 (C-4), 136.89 (C-5), 44.45 (2NCH₂), 13.13 (2Me), and aromatic C; m/z 324 (M⁺). (5): i.r. ν (C-N) 1665 cm⁻¹; ¹H n.m.r. ([²H₆]Me₂SO, Me₄Si) δ 8.08–7.76 (2H, m), 7.73-7.49 (3H, m), 3.50 and 3.43 (NMe₂, 2 × s), and 2.59 $(SMe, s); {}^{13}C{}^{1}H$ n.m.r. $([{}^{2}H_{6}]Me_{2}SO) \delta 175.60 (C-2), 149.95 (C-5),$ 114.38 (C-4), 43.31 and 40.48 (NMe₂), 19.56 (SMe), and aromatic C. (6a): i.r. v(C-N) 1620 cm⁻¹; ¹H n.m.r. (CDCl₃) δ 8.29–8.13 (2H, m), 7.45-7.08 (3H, m), 3.69 and 3.42 (2NCH₂, 2 × q, J7.0 Hz), 1.35 and 1.32 (2Me, $2 \times t$, J 7.0 Hz); ${}^{13}C{}^{1}H$ n.m.r. (CDCl₃) δ 174.77 (C-2), 142.01 (C-5), 136.75 (C-4), 49.54 and 45.84 (2NCH₂), 12.78 and 11.80 (2Me), and aromatic C; m/z 265 (M⁺). (6b): i.r. v(C-N) 1640 cm⁻¹; m/z 237.0280 (M^+). (7): i.r. v(C=O) 1708, 1651, 1633 cm⁻¹; ¹H n.m.r. (CDCl₃) & 8.27-7.97 (2H, m), 7.58-7.30 (3H, m), 3.40 (2NMe, s), and 2.53 (SMe, s); ¹³C{¹H} n.m.r. (CDCl₃) & 181.28 (C-5), 162.94 and 158.19 (2C=O), 151.31 and 150.58 (C-2, C=O), 114.91 (C-3), 94.64 (C-6), 28.07 and 27.84 (2NMe), 19.43 (SMe), and aromatic C. (8): i.r. v(C=O) 1640, 1608 cm⁻¹; ¹H n.m.r. (CDCl₃) δ 7.97–7.77 (2H, m), 7.56–7.33 (3H, m), 2.64, 2.53, and 2.51 (3Me, 3 × s); ¹³C{¹H} n.m.r. (CDCl₃) δ 194.69 and 194.08 (2C=O), 179.03 (C-5), 148.19 (C-2), 114.67 (C-6), 114.43 (C-3), 32.52 and 29.28 (2Me), 18.89 (SMe), and aromatic C.



Similarly, anhydrocyclisation of dialkylamino(thiocarbonyloxy)phenylacetic acids⁴ of type (1) in the presence of carbon disulphide afforded the new mesoionic (**6b**—**e**)‡ of lower solubility (Table 1), whose constitutions were established by elemental analyses and spectroscopic data. Also, the negative solvatochromic effect to the longest wavelength $\pi \rightarrow \pi^*$ electronic transition in the u.v. spectrum of (**6b**) [λ_{max} . 361 (dioxane), 332 nm (methanol)] is in agreement with the highly polar ground state of mesoionic compounds.^{2,5} Obviously, the *in situ* formed mesoionic 1,3-oxathioles of type (2) were trapped during the reaction course by [3 + 2] cycloaddition to carbon disulphide with subsequent elimination of carbon oxysulphide from the intermediate (3) to give (6), as outlined in Scheme 1.

In an analogous one pot reaction of $(1; R = NEt_2)^{\ddagger}$ with acetic anhydride-triethylamine and phenyl isothiocyanate, novel 1,3-oxazolylium-4-thiolate (4) (Scheme 1) was generated in 45% yield, m.p. 209–210 °C (decomp.).‡

These mesoionic heteroarenes (6) offered two new approaches to 1,4-oxathiafulvene derivatives. For example, the reaction of (6b) with methyl iodide in methanol gave, after precipitation with diethyl ether, a 99% yield of (5), m.p. 186–187 °C (decomp.).‡ Subsequent reaction of the salt (5) with 1,3-dimethylbarbituric acid in a mixture of acetic



acid-pyridine produced the 1,4-oxathiafulvene derivative (7), m.p. 238—239 °C, yield 91% (Scheme 2).‡ Compound (7) was produced in 22% yield by first reacting (6d) with 1,3dimethylbarbituric acid in pyridine-1,5-diazabicyclo-[4.3.0]non-5-ene (DBN) and then methylating with methyl iodide.

Under analogous reaction conditions, as outlined in Scheme 2, (6d) and acetylacetone formed (8), m.p. 126.5—127.5 °C, yield 47%.‡

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