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 reactions[3] 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.

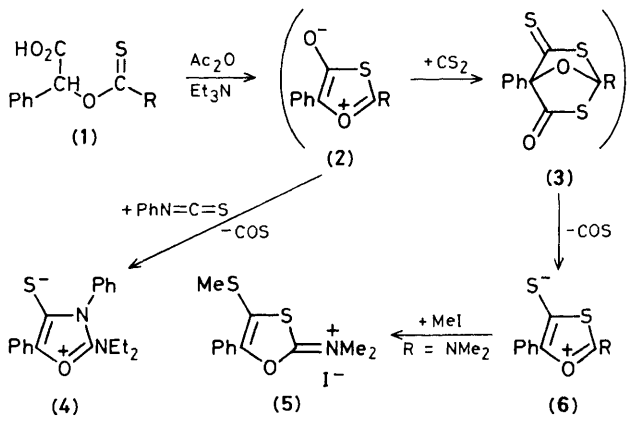
Thus, treatment of diethylamino(thiocarbonyloxy)phenylacetic acid† (**1**; R = NEt_2) with acetic anhydride–triethylamine in toluene in the presence of carbon disulphide at 50—60 °C produced yellow crystals of analytically pure 1,3-oxathiolylium-4-thiolate (**6a**) (Scheme 1, Table 1).‡

Table 1. 1,3-Oxathiolylium-4-thiolates (**6**) from (**1**).

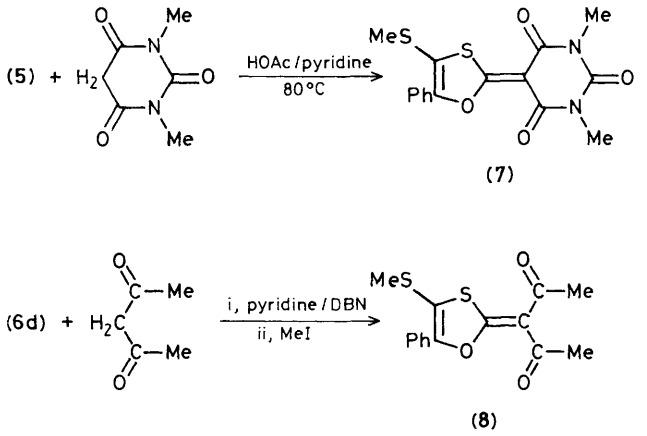
(**6**)	R	% Yield	M.p. (*t*/°C) (decomp.)	U.v. ($CHCl_3$) $\lambda_{max.}$/nm (log ε)
a	NEt_2	87	168—169	349 (4.21)
b	NMe_2	93	193.5—194.5	349 (4.20)
c	Pyrrolidino	85	190—191	349 (4.27)
d	Piperidino	87	167—168	350 (4.16)
e	Morpholino	56	178—179	349 (4.18)

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

‡ All new compounds gave satisfactory microanalytical data. *Spectroscopic data:* (**4**): i.r. ν(C–N) 1647 cm^{-1}; u.v. ($CHCl_3$) $\lambda_{max.}$ 345 nm (log ε 4.19); ^1H n.m.r. ($CDCl_3$) δ 8.33—8.17 (2H, m), 7.62—7.09 (8H, m), 3.27 ($2NCH_2$, q, *J* 7.0 Hz), and 1.10 (2Me, t, *J* 7.0 Hz); $^{13}C\{^1H\}$ n.m.r. ($CDCl_3$) δ 152.18 (C-2), 142.89 (C-4), 136.89 (C-5), 44.45 ($2NCH_2$), 13.13 (2Me), and aromatic C; *m/z* 324 (M^+). (**5**): i.r. ν(C–N) 1665 cm^{-1}; ^1H n.m.r. ($[^2H_6]Me_2SO$, Me_4Si) δ 8.08—7.76 (2H, m), 7.73—7.49 (3H, m), 3.50 and 3.43 (NMe_2, 2 × s), and 2.59 (SMe, s); $^{13}C\{^1H\}$ n.m.r. ($[^2H_6]Me_2SO$) δ 175.60 (C-2), 149.95 (C-5), 114.38 (C-4), 43.31 and 40.48 (NMe_2), 19.56 (SMe), and aromatic C. (**6a**): i.r. ν(C–N) 1620 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 8.29—8.13 (2H, m), 7.45—7.08 (3H, m), 3.69 and 3.42 ($2NCH_2$, 2 × q, *J* 7.0 Hz), 1.35 and 1.32 (2Me, 2 × t, *J* 7.0 Hz); $^{13}C\{^1H\}$ n.m.r. ($CDCl_3$) δ 174.77 (C-2), 142.01 (C-5), 136.75 (C-4), 49.54 and 45.84 ($2NCH_2$), 12.78 and 11.80 (2Me), and aromatic C; *m/z* 265 (M^+). (**6b**): i.r. ν(C–N) 1640 cm^{-1}; *m/z* 237.0280 (M^+). (**7**): i.r. ν(C=O) 1708, 1651, 1633 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 8.27—7.97 (2H, m), 7.58—7.30 (3H, m), 3.40 (2NMe, s), and 2.53 (SMe, s); $^{13}C\{^1H\}$ n.m.r. ($CDCl_3$) δ 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. ν(C=O) 1640, 1608 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 7.97—7.77 (2H, m), 7.56—7.33 (3H, m), 2.64, 2.53, and 2.51 (3Me, 3 × s); $^{13}C\{^1H\}$ n.m.r. ($CDCl_3$) 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.



Scheme 1



Scheme 2

Similarly, anhydrocyclisation of dialkylamino(thiocarbonyloxy)phenylacetic acids[4] 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**) [$\lambda_{max.}$ 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)† 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 1,3-dimethylbarbituric 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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