

New synthesis of 4,5-diaryl-1,3-oxathiol-2-ones

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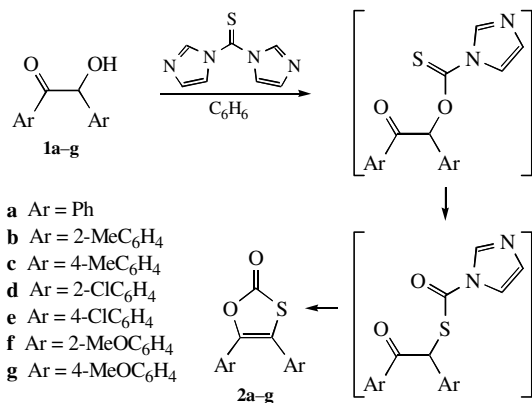
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A new method for the synthesis of 4,5-diaryl-1,3-oxathiol-2-ones by the reaction of 2-hydroxyethanone derivatives with 1,1'-thiocarbonyldiimidazole is proposed. The structure of 4,5-bis(4-methoxyphenyl)-1,3-oxathiol-2-one was studied by X-ray diffraction.

4,5-Diaryl-1,3-oxathiol-2-ones represent a poorly studied class of heterocycles, although they hold promise as fungicides.¹ The most popular methods for their synthesis include the reactions of halocarbonylsulfenyl halides with ketones,¹ the reactions of dibromoketones with potassium methylxanthate,² the oxidation of heterocyclic thiones,³ and the treatment of 2-thia-5-oxatitaniumcyclopent-3-ene with oxalyl chloride.⁴ These methods refer to particular cases; therefore, it is necessary to look for new general methods for the synthesis of 1,3-oxathiol-2-ones.

We found that substituted 4,5-diaryl-1,3-oxathiol-2-ones **2** are formed in the reactions of 2-hydroxyethanone derivatives **1** with 1,1'-thiocarbonyldiimidazole[†] (Scheme 1).



Scheme 1

The ready availability of the starting compounds and the high yields of products **2** (65–80%) attest to good prospects of this facile and convenient route for the preparation of 1,3-oxathiol-2-one derivatives. The reaction is general; it has been used to prepare a number of oxathiolones **2** with diverse aryl substituents.[†]

The putative scheme of transformation includes the acylation of acyloin **1**, intramolecular rearrangement of an intermediate to thioester, and cyclisation of the thioester furnishing 1,3-oxathiol-2-one **2**. This rearrangement follows, most likely, a mechanism similar to that described previously,^{5–6} and it is induced by a lower stability of the thiocarbonyl group compared to the carbonyl group, which is manifested as a more pronounced tendency for tautomeric transformations observed in thiocarbonyl compounds.

The structures of the products were proved by ¹H NMR spectroscopy and confirmed by elemental analysis data.[‡]

The molecular and crystal structures of 4,5-bis(4-methoxyphenyl)-1,3-oxathiol-2-one **2g** were confirmed by X-ray dif-

fraction.[§] The structure and conformation of a molecule of **2g** are shown in Figure 1. The 1,3-oxathiol-2-one fragment acts as a heterocyclic bridge between the two benzene rings. The Cambridge Crystal Data Centre (version 5.24, July 2003) (CCDC) contains no data on the structure of oxathiol-2-one rings; therefore, we present the key geometric characteristics of this ring: the 1,3-oxathiol-2-one ring S(3)C(2)O(6)C(4)C(5) is planar (to within ±0.01 Å). The bond lengths (in Å) are as follows: S(3)–C(2), 1.751(2); S(3)–C(4), 1.763(2); O(1)–C(2),

[‡] ¹H NMR spectra were recorded on Bruker AM-300 (300 MHz) and Bruker WM-250 (250 MHz) instruments in [D₆]DMSO. Melting points were measured on a Boetius hot stage and not corrected. The reaction mixtures were analysed and the purity of the products was checked using TLC on Merck Silica gel 60 F₂₅₄ plates using an AcOEt–hexane mixture (1:3) for elution.

2a: 78% yield, mp 119–120 °C (lit.,⁵ 56 °C, oil^{1,3}). ¹H NMR, δ: 7.35–7.60 (m, 10H, H_{Ar}). Found (%): C, 70.79; H, 3.93; S, 12.65. Calc. for C₁₅H₁₀O₂S (%): C, 70.85; H, 3.96; S, 12.61.

2b: 69% yield, mp 159–160 °C. ¹H NMR, δ: 2.11 (s, 6H, 2Me), 7.20–7.45 (m, 8H, H_{Ar}). Found (%): C, 72.38; H, 5.02; S, 11.42. Calc. for C₁₇H₁₄O₂S (%): C, 72.31; H, 5.00; S, 11.36.

2c: 72% yield, mp 178–179 °C. ¹H NMR, δ: 2.32 (s, 6H, 2Me), 7.35–7.50 (m, 8H, H_{Ar}). Found (%): C, 72.29; H, 4.97; S, 11.38. Calc. for C₁₇H₁₄O₂S (%): C, 72.31; H, 5.00; S, 11.36.

2d: 78% yield, mp 180–181 °C. ¹H NMR, δ: 7.40–7.65 (m, 8H, H_{Ar}). Found (%): C, 55.79; H, 2.50; Cl, 21.97; S, 9.85. Calc. for C₁₅H₈Cl₂O₂S (%): C, 55.74; H, 2.49; Cl, 21.94; S, 9.92.

2e: 83% yield, mp 152–153 °C. ¹H NMR, δ: 7.55–7.65 (m, 8H, H_{Ar}). Found (%): C, 55.71; H, 2.51; Cl, 21.98; S, 9.93. Calc. for C₁₅H₈Cl₂O₂S (%): C, 55.74; H, 2.49; Cl, 21.94; S, 9.92.

2f: 74% yield, mp 159–160 °C. ¹H NMR, δ: 3.48 (s, 6H, 2OMe), 7.05–7.15 (m, 4H, H_{Ar}), 7.40–7.55 (m, 4H, H_{Ar}). Found (%): C, 64.98; H, 4.48; S, 10.25. Calc. for C₁₇H₁₄O₄S (%): C, 64.95; H, 4.49; S, 10.20.

2g: 76% yield, mp 149–150 °C (lit.,⁴ 133–135 °C). ¹H NMR, δ: 3.72 (s, 3H, OMe), 3.74 (s, 3H, OMe), 6.90–7.00 (m, 4H, H_{Ar}), 7.20–7.30 (m, 4H, H_{Ar}). Found (%): C, 64.91; H, 4.48; S, 10.22. Calc. for C₁₇H₁₄O₄S (%): C, 64.95; H, 4.49; S, 10.20.

[§] Crystal data for **2g**: at T = 163 K, the crystals of C₁₇H₁₄O₄S are monoclinic, space group P2₁/c: a = 10.735(3), b = 12.379(3), c = 11.284(3) Å, β = 98.22(2)°, V = 1484.1(7) Å³, Z = 4, M = 314.34, d_{calc} = 1.407 g cm^{−3}. The unit cell parameters and the intensities of 2935 independent reflections were measured on a Syntex P2₁ diffractometer (MoKα, graphite monochromator, θ/2θ-scan mode in the 2.46 ≤ θ ≤ 26.05° range). The structure was solved by the direct method, which revealed all non-hydrogen atoms, and refined by full-matrix least-squares in the anisotropic approximation for non-hydrogen atoms. The hydrogen atoms were objectively revealed by difference electron density synthesis and refined isotropically by least-square calculations. The final R-factors for 1984 reflections with I > 2σ(I) were R₁ = 0.041, wR₂ = 0.114. For all independent reflections, R₁ = 0.082, wR₂ = 0.124. The calculations were performed using the Siemens P3/PC⁷ and SHELXTL PLUS 5⁸ program packages.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 221792. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2004.

[†] General procedure for the preparation of 4,5-bis(aryl)-1,3-oxathiol-2-ones **2a-g**. A mixture of an appropriate 2-hydroxy-1,2-bis(aryl)ethan-1-one (1 mmol) (commercially available or prepared by known procedures⁹) and 1,1'-thiocarbonyldiimidazole (1.5 mmol) in 5 ml of benzene was refluxed for 5–10 h (TLC monitoring). The reaction mixture was cooled, washed with water, 10% HCl, and again with water and dried with MgSO₄. The solvent was concentrated *in vacuo*. The residue was recrystallised from ethanol.

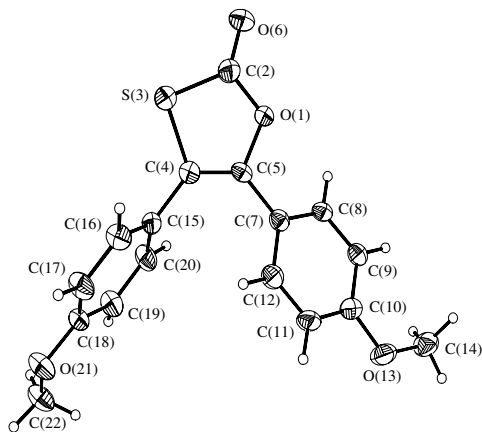


Figure 1 Structure and conformation of molecule **2g**.

1.359(3); O(1)–C(5), 1.412(2) (single bonds); O(6)–C(2), 1.199(3); C(4)–C(5), 1.336(3) (double bonds). No electron density delocalisation is found in the ring. A notable feature of the molecular conformation of **2g** is a difference between the degrees of rotation of the two benzene rings relative to the 1,3-oxathiol-2-one ring; in particular, the benzene ring on the O(1) side is rotated through 24.6° with respect to the 1,3-oxathiol-2-one ring, while the benzene ring on the S(3) side, through 61.5° . Both methoxy groups are virtually coplanar with the corresponding benzene ring planes, the C(9)–C(10)–O(13)–C(14) and C(17)–C(18)–O(21)–C(22) torsion angles being only 2.3 and 1.6° , respectively.

Thus, we developed a new facile method for the synthesis of 4,5-diaryl-1,3-oxathiol-2-ones by the reaction between substituted 2-hydroxyethan-1-ones with 1,1'-thiocarbonyldiimidazole.

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