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Michael R. Probert, Christopher A. Ramsden, Stephen P. Stanforth

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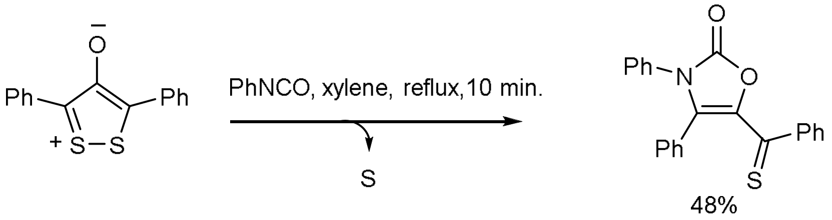


Addition of phenylisocyanate to 3,5-diphenyl-1,2-dithiolium-4-olate gives a thioketone.

Michael R. Probert,[a] Christopher A. Ramsden[b] and Stephen P. Stanforth[c]*

[a] School of Chemistry, Bedson Building, Newcastle University, Newcastle-upon-Tyne, NE1 7RU, UK
[b] Lennard-Jones Laboratories, School of Physical and Geographical Sciences, Keele University, Staffordshire, ST5 5BG, UK
[c] Department of Applied Sciences, University of Northumbria, Newcastle-upon-Tyne, NE1 8ST, UK

* steven.stanforth@northumbria.ac.uk.

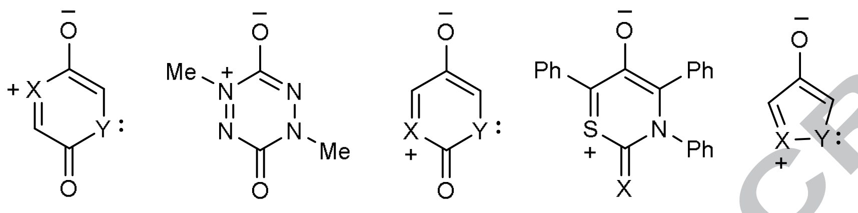
Abstract: The Type B mesoionic heterocycle, 3,5-diphenyl-1,2-dithiolium-4-olate, reacts with phenylisocyanate producing a thioketone derivative rather than a pseudo-semi-conjugated heterocyclic mesomeric betaine. The structure of the thioketone product was confirmed by an X-ray crystallographic investigation.

Keywords: mesomeric betaine, mesoionic, semi-conjugated

Only two examples (**4**, X = O, S, Fig. 1) of six-membered Class 5 heterocyclic mesomeric betaines (HMBs)[1,2] have been described in the literature. A claim,[3] based on unpublished work by Ollis and Morgan,[4] suggested that the green crystalline product obtained from the five-membered Class 5 HMB **6** and phenylisocyanate is the six-membered pseudo-semi-conjugated HMB **4** (X = O). We have reinvestigated this product and now report a revision of the published structure.

A classification of heterocyclic mesomeric betaines has recently been proposed from which five discrete classes of HMB are identified.[1,2] This classification system has enabled the similarities and differences in the chemistry and properties of a diverse range of HMBs to be rationalised. Two classes, semi-conjugated (Class 3) and pseudo-semi-conjugated (Class 5) HMBs, were not recognised as discrete types of heterocycle in an earlier classification system.[3] A feature of these heterocycles of some interest is the observation that (i) they are associated with a higher degree of classical and magnetic aromaticity but (ii) lower thermodynamic stability than their corresponding isomeric heterocycles, including those possessing fully covalent rings.[2,5]

The formulae **1** and **3** (Fig. 1), in which the heteroatoms X and Y each contribute 2π-electrons to the molecules' π-electron system, are general examples of six-membered semi-conjugated HMBs (structure **1**) and pseudo-semi-conjugated HMBs (structure **3**). To the best of our knowledge, heterocycle **2** is the only recorded example of a semi-conjugated HMB of general structure **1;** this structure was confirmed by X-ray crystallography.[6] As far as we are aware, only two examples (heterocycles **4**, X = O, S) of pseudo-semi-conjugated HMBs related to structure **3** have been disclosed.[4,7] In contrast to the 6-membered heterocycles **1** and **3**, the 5-membered Type B mesoionic heterocycles,[8,9] as represented by the general formula **5**, provide numerous examples of pseudo-semi-conjugated HMBs. In view of the relative paucity of structural information relating to the 6-membered heterocycles **1** and **3** and their potentially interesting properties, [2,5] we report in this Letter a re-investigation into the reported synthesis of heterocycle **4** (X = O).



1 **2** **3** **4** **5**

Figure 1. Semi-conjugated and pseudo-semi-conjugated HMBs.

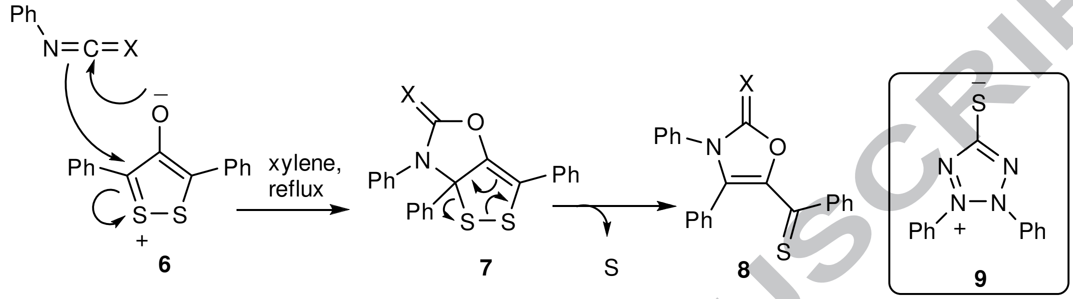
The Type B mesoionic compound, 3,5-diphenyl-1,2-dithiolium-4-olate **6**, was prepared by the reaction of 1,1,3-tribromo-1,3-diphenylpropane-2-one with potassium ethylxanthate in DMF at room temperature following a literature procedure.[10] Compound **6** was heated with phenylisocyanate in xylene at reflux, producing a green compound[11] for which the structures **4** (X = O)[4] and **8** (X = O)[12] had previously been assigned (Scheme 1). An X-ray crystallographic investigation (Fig. 2) has showed the structure of the green compound to be the thioketone derivative **8** (X = O),[13] confirming Rowson's original structural assignment.[12] The thioketone derivative **8** (X = O) adopts a Z'=2 structure in the Pbca space group. The model shows a network of weak hydrogen bonds pervading the system. The two independent molecules are related by non-crystallographic inversion with the sense of rotation of the phenyl rings, to the central plane, in opposite orientations.

The spectroscopic properties are also consistent with the thioketone structure **8** (X = O).[11] In particular, the infrared spectrum shows absorptions consistent with the presence of both thione (1359 cm^{-1}) and keto (1780 cm^{-1}) functional groups. Additionally, the green colour is consistent with its formulation as a thioketone derivative, e.g. thiobenzophenone is blue.[14] Similar green products reported by Rowson using 4-methylphenyl- , 4-chlorophenyl- and 2-naphthylisocyanate undoubtedly have the corresponding thioketone structures, correctly assigned by Rowson.[12]

The actual product **8** (X = O) is readily rationalised by the formation of adduct **7** (X = O), possibly in two steps, followed by opening of the dithiolene ring and elimination of sulfur (Scheme 1). Cycloadditions analogous to that proposed for the formation of product **8** (X = O) can be found in the chemistry of dehydrodithizone **9** which gives analogous bicycloadducts with the electrophilic dipolarophiles tetraphenylcyclopentadienone and dimethyl acetylenedicarboxylate, followed by opening of the original ring.[3,15]

Rowson also obtained a crystalline product (dark green needles, mp 201-203 ^{o}C (decomp.)) using phenylisothiocyanate instead of phenylisocyanate.[12] This product shows only the thione absorption (1360 cm^{-1}) with no evidence of a carbonyl group. This is almost certainly the thione **8** (X = S), as originally formulated by Rowson,[12] and not the HMB **4** (X = S), as later claimed.[7]

In conclusion, we have shown that the product obtained from the reaction of 1,2-dithiolium-4-olate **6** and phenylisocyanate is thioketone **8** (X = O), as proposed in the original unpublished study by Rowson.[12] The product formed using phenylisothiocyanate almost certainly has the analogous thioketone structure **8** (X = S) proposed by Rowson.[12] As far as we are aware, this means that no examples of the Class 5 HMBs of general structure **3** or their aza analogues are known. There is no reason why stable derivatives of this type should not be accessible and they present a challenging gap in the heterocyclic literature.



Scheme 1. A potential pathway for the reaction of compound **6** with phenylisocyanate and phenylisothiocyanate.

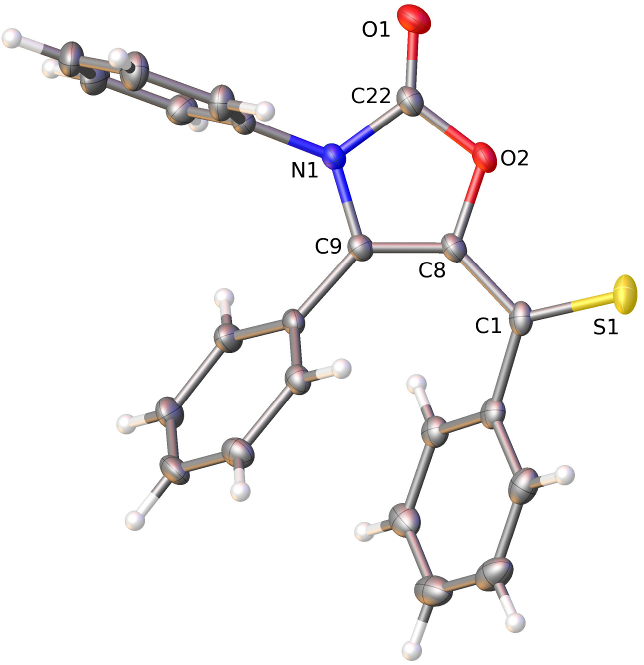


Figure 2. One of the independent molecular units from the single crystal X-ray structure of heterocycle **8** (X = O). Anisotropic displacement parameters are shown at the 50% probability level.

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11. Xylene (10 mL) was added to heterocycle **6** (0.20 g, 0.70 mmol) giving a purple mixture. Phenylisocyanate (0.20 mL, 1.85 mmol) was then added and the mixture heated at reflux (isomantle) with gentle agitation for 10 minutes. During the heating period, the colour of the mixture gradually changed from purple to green. The mixture was filtered whilst hot and green crystals of compound **8** (X = O) (0.14 g, 48%), mp 198-199 ^{o}C, were produced almost immediately from the cooling filtrate. Ref. 4 reports mp 199-202 ^{o}C and ref. 12 reports mp 199-200.5 ^{o}C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.44-7.41 (2H, m, ArH), 7.36-7.30 (3H, m, ArH), 7.22-7.14 (4H, m, ArH), 7.05-6.99 (4H, m, ArH), 6.96-6.91 (2H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 212.9, 152.7, 145.2, 142.5, 133.9, 132.7, 131.1, 130.1, 129.9, 129.4, 129.0, 128.7, 128.4, 127.7, 127.2, 126.1; IR ν_{max} (diamond anvil) 1780, 1556, 1486, 1390, 1359, 1230, 1132, 1056 cm^{-1}; HRMS found 358.0901. $C_{22}H_{16}NO_2S$ $[M+H]^+$ requires 358.0896; λ_{max} (MeOH) 390 nm (ε 9810). Copies of NMR spectra are given in the supplementary information.
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- The reaction of phenylisocyanate with a mesoionic heterocycle produces a novel thioketone
- The structures of products from similar reactions to that above have been either corrected or confirmed
- X-ray crystallography and spectral data confirm the thioketone structure