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Mesoionic Derivatives of the 1,3-Dithiole System

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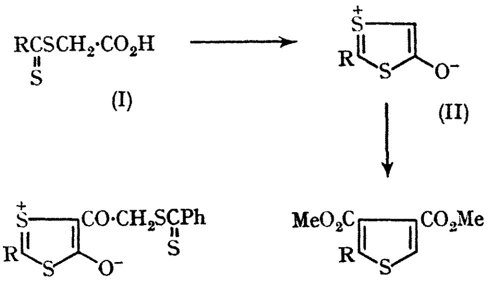
Summary Anhydro-5-hydroxy-2-phenyl-1,3-dithiolium hydroxide has been synthesized and the structure of the product previously described as this compound has been elucidated.

Numerous examples of mesoionic systems containing nitrogen, oxygen, and sulphur atoms in various combinations have been described.[1] It should be possible to obtain mesoionic compounds containing endocyclic sulphur atoms, a system of particular interest being the 1,3-dithiole system. Ohta and Sugiyama[2] have described the preparation of such a system, in particular, anhydro-5-hydroxy-2-phenyl-1,3-dithiolium hydroxide (II; R = Ph) obtained from thiobenzoylthioglycollic acid (I) with acetic anhydride and boron trifluoride. Several 4-phenyl analogues of (II) have also been described recently.[3] Our results, which show that the product previously described as (II) is, in fact, anhydro-5-hydroxy-2-phenyl-4-(thiobenzoylthiomethylcarbonyl)-1,3-dithiolium hydroxide (III), are thus of especial interest. We also report synthesis of (II) and of its 2-*p*-methoxyphenyl analogue.

Treatment of thiobenzoylthioglycollic acid (I; R = Ph) (2·0 g.) with acetic anhydride (2 ml.) and triethylamine (5 ml.) at 0—10° gave, contrary to the previous report,[2a] glistening scarlet needles (77%) of the mesoionic compound† (II; R = Ph) [m.p. 113—115° decomp.; *m/e* 194 (40%, M^+); n.m.r. ($CDCl_3$) τ 3·94 (s, 1, 4-H), 2·49 (m, 5, Ph); ν_{max} (KBr) 1610 (C=O) cm.$^{-1}$; λ_{max} (anhydrous MeOH) 203, 220, 265, 285, and 325 nm. (log ϵ 4·50, 4·24, 3·96, 3·89, and 3·46)]. In an analogous fashion, anhydro-5-hydroxy-2-*p*-methoxyphenyl-1,3-dithiolium hydroxide (II; R = *p*-Me OC_6H_4 was obtained from the appropriate dithioglycollic acid as brilliant, scarlet-red needles (80%) [m.p. 143—145° decomp.; *m/e* 224 (32% M^+); n.m.r. ($CDCl_3$) τ 6·12 (s, 3, OCH_3), 4·10 (s, 1, 4-H), 3·12—2·97 (AB, d, 2, *J* 9·00 Hz., aromatic), 2·49—2·34 (AB, d, 2, *J* 9·00 Hz., aromatic); ν_{max} (KBr) 1600 (C=O) cm.$^{-1}$; λ_{max} (anhydrous MeOH) 200, 230, 255, and 330 nm. (log ϵ 4·36, 4·21, 3·83, and 3·83)]. These mesoionic compounds were moderately sensitive in solution to traces of moisture and optimum results were obtained only using very pure dithioglycollic acids and working under "dry-box" conditions with anhydrous solvents. They are quite stable in the dry, solid state.



(I)

(II)

(III)

(IV)

It has been shown previously[4] that carbonyl sulphide can be eliminated readily in the 1,3-dipolar cycloaddition-type reaction of anhydro-5-hydroxythiazolium hydroxides with acetylenic dipolarophiles. A similar reaction has been observed[5] between the 4-phenyl analogue of (II) and dimethyl acetylenedicarboxylate with the formation of substituted thiophens. Under these conditions (II) and its *p*-methoxyphenyl analogue readily formed the thiophens (IV) with elimination of carbonyl sulphide.[6] This confirmed structure (II) for our product. Thus, from (II; R = Ph), a 40% yield of dimethyl 2-phenylthiophen-3,4-dicarboxylate (IV; R = Ph) was obtained [cream needles, m.p. 70—71°; *m/e* 276 (38% M^+); n.m.r. ($CDCl_3$) τ 6·19, [s, 3, 3- (or 4-)CO_2CH_3], 6·17 [s, 3, 3-(or 4-)CO_2CH_3], 2·57 (m, 5, Ph), 2·02 (s, 1, 5-H); ν_{max} (KBr) 1725 (C=O) cm.$^{-1}$; λ_{max} (MeOH) 207, 230, and 275 nm. (log ϵ 4·28, 4·28, and 3·91)] and from (II; R = *p*-$MeOC_6H_4$), dimethyl 2-*p*-methoxyphenylthiophen-3,4-dicarboxylate (IV; R =*p*-Me

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† Satisfactory analytical data were obtained for all new products and their mass spectral fragmentation patterns were consistent with the assigned structures.

OC_6H_4) was obtained in 47% yield [cream needles, m.p. 100—101°; *m/e* 306 (70% M^+); n.m.r. τ 6·17 (s, 6, 3- and 4-CO_2CH_3), 6·15 (s, 3, OCH_3), 3·17—3·02 (AB,d, 2, *J* 9·00 Hz., aromatic), 2·64—2·49 (AB,d, 2, *J* 9·00 Hz., aromatic), 2·10 (s, 1, 5-H); ν_{max} (KBr) 1725 (s), 1720 (m) (C=O) cm.$^{-1}$; λ_{max} (MeOH) 205, 240, and 275 nm. (log ε 4·47, 4·41, and 4·38)].

Our spectral data for (II), together with that of its 4-phenyl analogue,[3] indicated that the structure of the product previously assumed to be (II), required revision. Furthermore, this product was isolated *via* an aqueous work-up procedure and our results indicated that the compound (II) was extremely sensitive to moisture. Reaction of thiobenzoylthioglycollic acid (I) with acetic anhydride and boron trifluoride etherate over several minutes gave a product identical with that described earlier.[2a] Longer reaction times resulted in considerable polymer formation. The product had *M* = 388 [*m/e* 388 (5% M^+)] and n.m.r. data ($CDCl_3$) indicated the presence of two phenyl groups (τ 2·52, m, 10) and two methylene protons which appeared as two AB doublets with *J* 16·50 Hz. at τ 5·67—5·92 and 5·99—6·25. These data clearly establish the structure of the product obtained in the presence of boron trifluoride–acetic anhydride as (III).

Similar acylated products were obtained in the preparation of mesoionic oxazolones[7] and agreement is noted between the main spectral features of this system and that discussed above.

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[1] A review describing earlier aspects of this topic is: W. Baker and W. D. Ollis, *Quart. Rev.*, 1957, **11**, 15. Recent references can be found in: A. R. McCarthy, W. D. Ollis, and C. A. Ramsden, *Chem. Comm.*, 1968, **499**; R. Grashey, M. Baumann, and W. D. Lubos, *Tetrahedron Letters*, 1968, 5877; K. T. Potts and C. Sapino, *Chem. Comm.*, 1968, 672.

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