Mesoionic Compounds of the Thiazole Series: *anhydro*-2,3-Diphenyl-4-hydroxythiazolium Hydroxide

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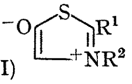
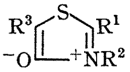
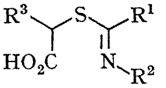
Summary *anhydro*-2,3-Diphenyl-4-hydroxythiazolium hydroxide and its 3-*p*-chlorophenyl analogue have been synthesized for the first time and revised structures assigned to the products previously described as these mesoionic compounds.

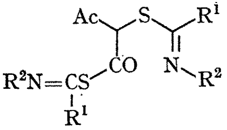
Two isomeric mesoionic systems containing the thiazole nucleus are possible, the *anhydro*-2,3-disubstituted-5-hydroxythiazolium hydroxide system (I) and the *anhydro*-2,3-disubstituted-4-hydroxythiazolium hydroxide system (II). The ease with which the former system underwent 1,3-dipolar cycloadditions has been described.[1] System (II) might be expected to undergo Diels–Alder type cycloadditions.[2]

anhydro-2,3-Diphenyl-4-hydroxythiazolium hydroxide (II; R^1 = R^2 = Ph; R^3 = H) has been described[3] as colourless needles, m.p. 195—196°, and was prepared by Ac_2O–Et_3N cyclization of the intermediate acid (III; R^1 = R^2 = Ph; R^3 = H), itself obtained from thiobenzanilide and bromoacetic acid. We confirmed these physical characteristics but the spectral properties of the product were incompatible with structure (II). Strong i.r. absorptions at 1725, 1680, and 1590 cm^{-1} suggested the presence of two carbonyl groups and a $>C{=}N-$ group; n.m.r. τ 8·21 (s, 3H, CO·CH_3), 5·30 (s, 1H, $-\overset{|}{\underset{|}{C}}H$) and 2·46 (m, 20H, ArH); u.v., λ_{max} (MeOH) 201 (log ϵ 4·83), 240sh (4·10) and 267sh nm (3·58). The molecular weight† of the product was established as 508 and analytical data indicated that the molecular formula was $C_{30}H_{24}N_2O_2S_2$. Reaction of this product with hot acetic anhydride[3] readily gave orange plates, m.p. 250—252° (decomp.) [ν_{max} (KBr) 1650 (COMe), 1600 cm^{-1} (CO); λ_{max} (MeOH) 200 (log ϵ 4·25), 237sh (3·98), 263 (4·10), 401 nm (4·04); n.m.r. ($CDCl_3$) τ 7·37 (s, 3H, CO·CH_3), 2·63 (m, 10H, ArH); M^+, *m/e* 295 (29%)] whose spectral characteristics are consistent with its formulation as *anhydro*-5-acetyl-2,3-diphenyl-4-hydroxythiazolium hydroxide (II; R^1 = R^2 = Ph; R^3 = CO·CH_3).


(I)


(II)


(III)


(IV)

The above data, and the close relationship of the acetyl product, suggested that the structure of the product previously thought to be the mesoionic compound was, in fact, 2-mercapto-1-thioacetoacetic acid, anhydrosulphide with *N*-phenylthiobenzimidic acid, *N*-phenylbenzimidate (IV; R^1 = R^2 = Ph).

Analogous results were obtained from the intermediate acid (III; R^1 = Ph; R^2 = *p*-ClC_6H_4; R^3 = H) derived from

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† Determined by mass spectroscopy.

p-chlorothiobenzanilide and bromoacetic acid. The product (IV; R^1 = Ph: R^2 = *p*-ClC_6H_4) [colourless needles, m.p. 190—192° (lit.[3] 165—166°); ν_{max} (KBr) 1720, 1660, 1490 cm.$^{-1}$; λ_{max} (MeOH) 202 (log ϵ 4·84), 246sh nm (4·22); n.m.r. ($CDCl_3$) τ 8·20 (s, 3H, CO·CH_3), 5·25 (s, 1H, $-\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{H}$), 2·60 (m, 18H, ArH)] gave an acetyl derivative [orange plates, m.p. 240—242°; ν_{max} (KBr) 1660, 1600 cm.$^{-1}$; λ_{max} (MeOH) 203 (log ϵ 4·33), 225 (4·14), 263 (4·02), 403 nm (3·92); n.m.r. ($CDCl_3$) τ 7·35 (s, 3H, CO·Me), 2·55 (m, 9H, ArH); M^+, *m/e* 330 (20%)].

Variation of the reaction conditions which yielded product (IV) has resulted in the formation of *anhydro*-2,3-diphenyl-4-hydroxythiazolium hydroxide (II; R^1 = R^2 = Ph; R^3 = H) and its 3-*p*-chlorophenyl analogue (II; R^1 = Ph; R^2 = *p*-ClC_6H_4; R^3 = H) for the first time. The intermediate acid (III) was treated with the minimum volume of Ac_2O–Et_3N (1 : 3), shaken at room temperature for several minutes, and crystallization then induced by scratching. Anhydrous ether was added and the product‡ was collected under Dry-box conditions. *anhydro*-2,3-Diphenyl-4-hydroxythiazolium hydroxide (II; R^1 = R^2 = Ph; R^3 = H) formed orange yellow needles (38%), m.p. 113—115° (decomp.) [ν_{max} (KBr) 1610 (CO) cm^{-1}; λ_{max} (anhydrous MeOH) 202 (log ϵ 4·72), 240 (4·27), 350 nm (2·62); n.m.r. ($CDCl_3$) τ 4·43 (s, 1H, 5-H), 2·72 (m, 10H, ArH); M^+, *m/e* 253 (29%)]. The product is extremely sensitive to moisture and undergoes decomposition on standing in the atmosphere. In a similar fashion *anhydro*-3-*p*-chlorophenyl-4-hydroxy-2-phenylthiazolium hydroxide (II; R^1 = Ph; R^2 = *p*-ClC_6H_4; R^3 = H) was obtained from the corresponding acid (III) as orange–yellow needles (35%), m.p. 115—116° (decomp.) [ν_{max} (KBr) 1620 (CO) cm^{-1}; λ_{max} (anhydrous MeOH) 200 (log ϵ 4·22), 220sh (3·87), 242 (3·66), 385 nm (3·46); n.m.r. ($CDCl_3$) τ 4·43 (s, 1H, 5-H), 2·68 (m, 9H, ArH); M^+, *m/e* 288 (25%)].

Reaction with acetic anhydride converted both these mesoionic compounds into acetyl derivatives, identical with those obtained from the respective (IV) and acetic anhydride.

These results are of particular importance in view of the ready reaction of α-bromophenylacetic acid under the original reaction conditions[3] to give the expected *anhydro*-4-hydroxy-2,3,5-triphenylthiazolium hydroxide (II; R^1 = R^2 = R^3 = Ph). Similar instances in which the mesoionic compound is only obtained by use of extremely mild and, apparently, sensitive reaction conditions have been reported.[4]

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‡ Satisfactory analytical and mass spectral data were obtained for these new products.

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[2] K. T. Potts, E. Houghton, and U. P. Singh, *Chem. Comm.*, following communication.

[3] M. Ohta, H. Chosho, C. Shin, and K. Ichimura, *J. Chem. Soc. Japan*, 1964, **85**, 440; for related derivatives see also H. Chosho, K. Ichimura, and M. Ohta, *Bull. Chem. Soc. Japan*, 1964, **37**, 1670; M. Ohta, K. Yoshida, and S. Sato, *ibid.*, 1966, **39**, 1269; K. Ichimura and M. Ohta, *ibid.*, 1965, **38**, 707.

[4] K. T. Potts and U. P. Singh, *Chem. Comm.*, 1969, 569.