1,3-Dipolar Cyclo-addition of Mesoionic Anhydro-2-aryl-5-hydroxy-3-methylthiazolium Hydroxides

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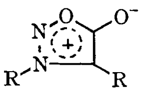
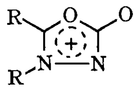
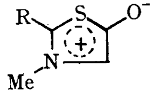
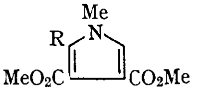
1,3-DIPOLAR CYCLO-ADDITIONS utilizing mesoionic ring systems have been shown to occur readily with 3,4-disubstituted anhydro-5-hydroxy-1,2,3-oxadiazolium hydroxides (I), particularly with acetylenic[1] and ethylenic[2] dipolarophiles. The isomeric system, 2,3-disubstituted anhydro-5-hydroxy-1,3,4-oxadiazolium hydroxide (II), has also been shown to undergo cyclo-addition with ethyl phenylpropiolate,[1] although less readily. Similar behaviour was observed with the anhydro-5-hydroxy-3-substituted 1,2,3,4-oxatriazolium hydroxide ring system.[1] 2,3,4-Trisubstituted anhydro-5-hydroxy-oxazolium hydroxides also undergo smooth 1,3-dipolar cyclo-addition with a variety of acetylenic dipolarophiles.[3] All these reactions involve elimination of carbon dioxide from the initial mesoionic system.


(I)


(II)


(III)


(IV)

We report the first example of a mesoionic 1,3-dipolar cyclo-addition in which carbonyl sulphide was used as the leaving group. Reaction of anhydro-5-hydroxy-3-methyl-2-phenylthiazolium hydroxide[4] (III; R = Ph) [cream prisms, m.p. 144—146°, ν_{max} (KBr) 1602 and 1525 cm.$^{-1}$, λ_{max} (MeOH) 204, 236, 280, and 358 mμ (log ϵ 4·04, 3·71, 3·32, and 3·59), n.m.r. ($CDCl_3$) τ 6·25 (s, N-Me), 3·80 (s, 4-H), and 2·55 (S, 5, aromatics), *m/e* 191 (53% M^+)] with dimethyl acetylenedicarboxylate in anhydrous benzene under reflux for 15 hr. gave dimethyl 1-methyl-2-phenylpyrrole-3,4-dicarboxylate† (IV; R = Ph) (66%) [flakes, m.p. 117—118°, ν_{max} (KBr) 1700 cm.$^{-1}$, λ_{max} (MeOH) 208 and 262 mμ (log ϵ 4·47 and 4·09), n.m.r. ($CDCl_3$) τ 6·60 (s, 3-CO_2Me), 6·40 (s, 4-CO_2Me), 6·20 (s, N-Me), 2·80 (s, 5-H), and 2·65 (s, 5, aromatics), *m/e* 273 (56% M^+)]. Similarly, (III; R = *p*-ClC_6H_4) [cream needles, m.p. 159—161°, ν_{max} (KBr) 1620 and 1510 cm.$^{-1}$, λ_{max} (MeOH) 204, 245, 270, and 360 mμ (log ϵ 4·15, 3·90, 3·38, and 3·34) n.m.r. [$^2H_6$]dimethyl sulphoxide τ 6·20 (s, N-Me), 3·6 (s, 4-H), and 2·40 (s, 4, aromatics), *m/e* 225 (53% M^+)] gave the corresponding pyrrole (IV; R = *p*-ClC_6H_4) (50%), [m.p. 108—109°; ν_{max} (KBr) 1700 cm.$^{-1}$ λ_{max} (MeOH) 224 and 266 mμ (log ϵ 4·13 and 4·05), n.m.r. ($CDCl_3$) τ 6·50 (s, 3-CO_2Me), 6·35 (s, 4-CO_2Me),

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† All products obtained gave satisfactory analytical data and their mass spectral fragmentation patterns were consistent with the assigned structures.

6·20 (s, N–CH_3), 2·80 (s, 5-H), and 2·65—2·70 (m, 4, aromatics); *m/e* 307 (40% M^+)].

This cyclo-addition occurs with great ease. The ready elimination of carbonyl sulphide is particularly interesting in view of the extreme reluctance of other mesoionic ring systems to undergo 1,3-dipolar cyclo-additions.[5] As would be expected, the introduction of an acetyl group[4] into the four position of (III) completely suppressed the ability of this mesoionic system to undergo cyclo-additions.

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