Interconversion of Mesoionic Ring Systems. The Conversion of Anhydro-2-aryl-5-hydroxy-3-methylthiazolium Hydroxides into Anhydro-2-aryl-4-mercapto-1-methyl-3-phenylimidazolium Hydroxides

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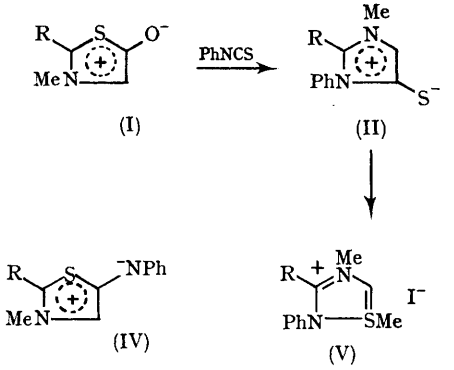
INTERCONVERSION of mesoionic ring systems offers both an important route to those systems which cannot readily be obtained by synthesis, as well as information regarding their relative reactivities. One method of effecting such interconversion, depending on a ring opening–ring closure sequence, has been demonstrated.[1] Treatment of anhydro-5-hydroxy-3-methyl-2-phenyl-1,3,4-oxadiazolium hydroxide with hydrogen sulphide in pyridine-chloroform was shown to give 1-methyl-1-thiobenzoyl hydrazine which underwent cyclization with phosgene to anhydro-5-hydroxy-3-methyl-2-phenyl-1,3,4-thiadiazolium hydroxide.[2]



We report a second method for effecting interconversion of mesoionic systems. Treatment of anhydro-5-hydroxy-3-methyl-2-phenylthiazolium hydroxide (I; R = Ph) with phenyl isothiocyanate in hot benzene readily gave anhydro-2,3-diphenyl-4-mercapto-1-methylimidazolium hydroxide (II; R = Ph) [yellow flakes (28%) m.p. 231—232°; λ_{max} (MeOH) 205, 235, and 325 $m\mu$ (log ϵ 4·48, 4·20, and 3·77); ν_{max}(KBr) 1600, 1500, 1475, and 1142 cm.$^{-1}$; n.m.r. ($CDCl_3$) τ 6·35 (s, N-Me), 3·10 (s, 5-H), and 2·60—2·70 (m, 10, aromatics); *m/e* 266 (41% M^+)] which yielded a methiodide (III; R = C_6H_4) [prisms, m.p. 216—217°; λ_{max} (MeOH) 208, 222, and 260 $m\mu$ (log ϵ 4·57, 4·50, and 3·98); ν_{max}(KBr) 1500 cm.$^{-1}$; n.m.r. ($CDCl_3$) τ 7·60 (s, S–Me_3), 6·05 (s, N-Me), 2·55—2·65 (m, 10, aromatics), and 2·05 (s, 5-H); *m/e* 266 (74% $[M - Me]^+$)].

Similarly, (I; R = p-ClC_6H_4) yielded (II; R = p-ClC_6H_4) [yellow prisms (33%), m.p. 229—231°; λ_{max} (MeOH) 202, 236, and 343 $m\mu$ (log ϵ 4·03, 3·99, and 3·49); ν_{max}(KBr) 1500 and 1150 cm.$^{-1}$; n.m.r. ($[^2H_6]$dimethyl sulphoxide) τ 6·40 (s, N-Me), 3·10 (s, 5-H), and 2·55—2·72 (m, 9, aromatics); *m/e* 300 (32% M^+)] which also readily formed a methiodide (III; R = p-ClC_6H_4) [prisms, m.p. 189—191°; λ_{max} (MeOH) 224 and 265 $m\mu$ (log ϵ 3·81 and 3·62); ν_{max} (KBr) 1500 cm.$^{-1}$; n.m.r. ($CDCl_3$) τ 7·58 (s, S-Me), 6·00 (s, N-Me), 2·10—2·50 (m, 9, aromatics), and 2·00 (s, 5-H); *m/e* 300 (64%

[M — Me]$^+$)]. Ready formation of a methiodide from (II) with the above characteristics† eliminates structure (IV) for these products.

Phenyl isothiocyanate has been shown[3] to undergo cyclo-addition reactions with 1,3-dipolar systems and this present reaction is analogous to the 1,3-dipolar cyclo-addition with an acetylenic dipolarophile reported.[4]

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

[1] A. R. McCarthy, W. D. Ollis, and C. A. Ramsden, *Chem. Comm.*, 1968, 499.

[2] See also K. T. Potts and C. Sapino, jun., *Chem. Comm.*, 1968, 672.

[3] R. Huisgen and A. Eckell, *Tetrahedron Letters*, 1960, 5; R. Huisgen, *Angew. Chem. Internat. Ed.*, 1963, **2**, 565, 633; R. Huisgen, R. Grashey, J. M. Vernon, and R. Kunz, *Tetrahedron*, 1965, **21**, 3311; 1966, **22**, 2400; J. E. Baldwin, G. V. Kaiser, and J. A. Romersberger, *J. Amer. Chem. Soc.*, 1964, **86**, 4509; 1965, **87**, 4114; J. E. Baldwin, *J. Org. Chem.*, 1967, **32**, 2438.

[4] K. T. Potts and D. N. Roy, preceding Communication.