

Carbenoid Intermediates in the Synthesis of Mesoionic Anhydro-4-hydroxythiazolium Hydroxides

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α -(Tosylhydrazono)phenylacetyl chloride and *N*-monosubstituted thioamides in dry, non-protic solvents and in the presence of Et₃N give representatives of the title mesoionic ring system in good to excellent yields; carbene or carbenoid type intermediates are most likely involved in these regiospecific cyclizations.

The potential for ylide formation by the reaction of a nucleophilic heteroatom with an electron-deficient species such as a carbene has been exploited recently in the formation of a stable carbonyl ylide, tetramethyluronium tetrakis(trifluoromethyl)cyclopentadienylide,¹ and also in the formation of the mesoionic anhydro-4-hydroxyoxazolium hydroxide system.² We have also been studying the use of appropriately substituted carbenes in the intramolecular generation of thiocarbonyl ylides, and this communication describes the application of carbene intermediates to the ready synthesis of the mesoionic anhydro-4-hydroxythiazolium hydroxide system.

α -(Tosylhydrazono)phenylacetyl chloride³ (1) (ν_{CO} 1740 cm⁻¹) and 3*H*-quinazoline-4-thione (2) in anhydrous Et₂O, when treated with two equivalents of Et₃N, gave, after stirring at room temperature for 12 hours, anhydro-3-hydroxy-2-phenylthiazolo[3,2-*c*]quinazolin-4-ium hydroxide (4; R = H)

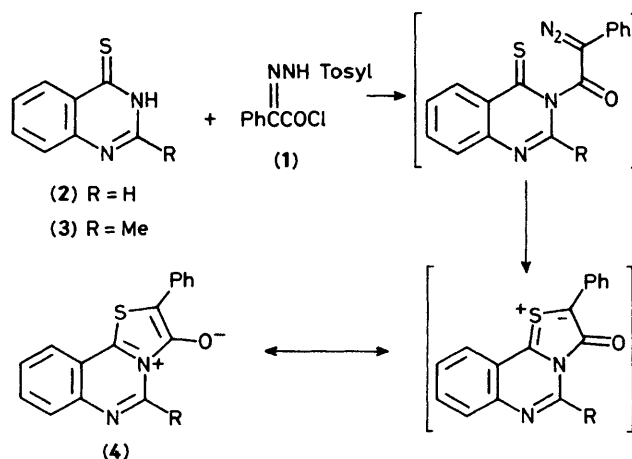
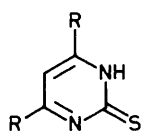


Table 1. Reactions of *N*-monosubstituted thioamides with (1).^a

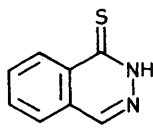
Thiazolium mesoionic system derived from compound	Crystal habit	Recrystallization solvent ^b	M.p. (°C)	Yield (%)	$\nu_{C=O}$ (cm ⁻¹)
(2)	Dark red needles	A	256—259	86	1635
(3)	Purple needles	B	198—200	86	1645
(5)	Red needles	B	190—192	60	1635
(6)	Dark red prisms	C	(decomp.) 198—201	93	1645
(7)	Dark red prisms	A	(decomp.) 258—262	93	1640
(8)	Orange needles	B	(decomp.) 248—252	80	1690, 1650
(9)	Orange prisms	C	(decomp.) 177—179	76	1615
(10)	Golden prisms	C	(decomp.) 154—156	88	1640

^a All new compounds reported had satisfactory analytical data ($\pm 0.4\%$ C, H, N) and known compounds had identical m.p.s, i.r., ¹H and ¹³C n.m.r. spectra with those prepared (ref. 5) previously by unambiguous routes. *M*⁺ consistent with the assigned structures were obtained for all compounds. ^b A = CHCl₃-hexane; B = EtOAc; C = Ac₂O-Et₂O.

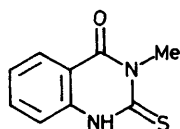


(5) R = Me

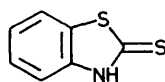
(6) R = H



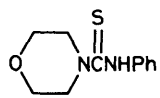
(7)



(8)



(9)



(10)

obtained as deep-red needles (86%) after recrystallization from chloroform-hexane, m.p. 256—259°C (lit.⁴ m.p. 262—264°C). Tetrahydrofuran, benzene, and methylene chloride may all be used as solvents, and bases such as NaH provide equally good results. Table 1 shows the variety of *N*-monosubstituted thioamides which react readily with (1). In all cases only one of the two possible mesoionic systems is

formed,[†] and the reaction is believed to involve an initial *N*-acylation as an intermediate *N*-acyldiazo compound can be detected in the reaction mixture ($\nu_{C=N_2}$ 2110—2080s, ν_{CO} 1675 cm⁻¹).

This intramolecular carbenoid-type cyclization provides an excellent synthetic route to anhydro-3-hydroxy-2-phenylthiazolium hydroxides. As α -keto acids are readily available, considerable potential exists for varying the substituents on the acetyl chloride.

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References

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[†] Formation of the alternative anhydro-5-hydroxythiazolium hydroxide system can be excluded by the presence of the PhCS⁺ ion, *m/z* 121, in the mass spectrum.