A New Synthetic Route to Mesoionic Thiazoles

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Summary Mesoionic thiazoles are obtained in good yield by the reaction of *gem*-dicyano epoxides with thioamides in a neutral medium.

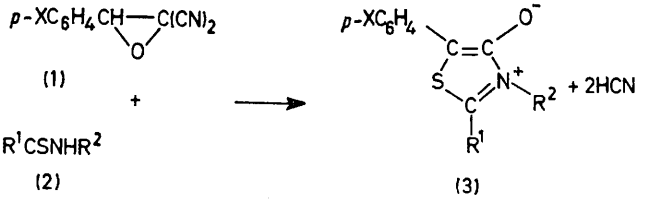
ANHYDRO-5-HYDROXYTHIAZOLIUM HYDROXIDES (**3**) are masked 1,3 dipoles and are useful synthetically in heterocyclic chemistry,[1] but only a few synthetic routes leading to them are known.[2] We report here a new synthetic route to the mesoionic compounds (**3**).

TABLE. Preparation of the mesoionic thiazoles (**3**)[a]

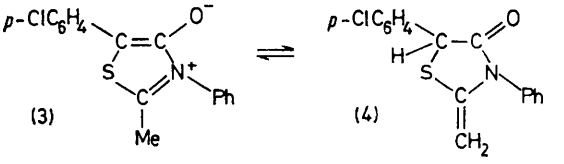
X	R^1	R^2	M.p. (*t*/°C)	Yield (%)	$\nu_{C=O}$/cm^{-1} (CCl_4)
H	Ph	Ph	270[b]	72	1630
Cl	Ph	Ph	300	94	1630
NO_2	Ph	Ph	273	70	1654
Cl	Ph	$PhCH_2$	168	65	1625
NO_2	Ph	$PhCH_2$	210	71	1638
Cl	Me	Ph	180	30	1716, 1628
NO_2	Me	Ph	280	60	1644

[a] Combustion analyses and mass spectra of the compounds herein are in agreement with this structure. [b] Ref. 5.

The *gem*-dicyano-epoxides[3] (**1**) react in solution in dioxan or acetone with stoicheiometric quantities of the thioamides (**2**) (Scheme 1).[4] In most cases the reaction is complete after 24 h at room temperature and the mesoionic thiazoles (**3**) are obtained after evaporation. They are usually deep red, with the ring carbonyl i.r. band in the



SCHEME 1



SCHEME 2. For (**3**), δ(Me) 2·48(s); for (**4**); δ(CH) 5·18(s), δ(CH_2) 4·34 (ABq, J_{AB} 2·5 Hz). All signals disappear on addition of CD_3CO_2D.

range[2] 1620—1650 cm^{-1} (Table). It is interesting that compound (**3**; X = Cl, R^1 = Me, R^2 = Ph) shows two carbonyl bands in solution in CCl_4, whereas the solid (Nujol mull) shows only one band, at 1623 cm^{-1}. Its n.m.r. spectrum ($CHCl_3$) shows the existence of a tautomeric equilibrium (**3**)⇌(**4**) (Scheme 2).

This result suggests that the compound obtained by Ohta *et al.*,[5] is not a mesoionic compound (**3**; X = H, R^1 = Me, R^2 = Ph). The unusually high value of the carbonyl band 1710 cm^{-1} (KBr) observed for this compound, is in best agreement with a tautomeric form similar to (**4**).

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[1] K. T. Potts, E. Houghton, and U. P. Singh, *Chem. Comm.*, 1969, 1129; *J. Org. Chem.*, 1974, **39**, 3627; K. T. Potts, J. Baum, and E. Houghton, *J. Org. Chem.*, 1974, **39**, 3631; S. Nakazawa, T. Kiyosawa, K. Hirakawa, and H. Kato, *J.C.S. Chem. Comm.*, 1974, 621.

[2] M. Ohta and H. Kato, 'Sydnones and Other Mesoionic Compounds,' in 'Non-benzoid Aromatics,' ed. J. P. Snyder, Academic Press, New York, 1969.

[3] The *gem*-dicyano-epoxides (**1**) were obtained quantitatively in a few minutes, by the reaction of NaClO with α-cyano-acrylonitriles: J. J. Pommeret and A. Robert, *Tetrahedron*, 1971, **27**, 2977.

[4] This reaction is comparable with the reaction of (**1**) and with thiourea, leading to 2-amino-4-thiazolinones. The two mechanisms must be similar; M. Ferrey, A. Robert, and A. Foucaud, *Compt. Rend.*, 1973, **277C**, 1153.

[5] M. Ohta, H. Chosho, C. Shin, and K. Ichimura, *J. Chem. Soc. Japan*, 1964, **85**, 440.