

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).

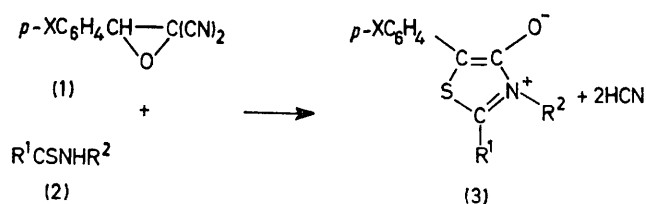
TABLE. Preparation of the mesoionic thiazoles (3)^a

X	R ¹	R ²	M.p. (t/°C)	Yield (%)	$\nu_{C=O}/\text{cm}^{-1}$ (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.

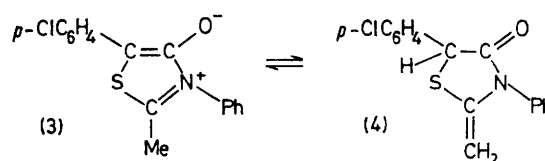
The *gem*-dicyano-epoxides³ (1) react in solution in dioxan or acetone with stoichiometric quantities of the

thioamides (2) (Scheme 1).⁴ In most cases the reaction is complete after 24 h at room temperature and the meso-



SCHEME 1

ionic thiazoles (3) are obtained after evaporation. They are usually deep red, with the ring carbonyl i.r. band in the



SCHEME 2. For (3), $\delta(\text{Me})$ 2.48(s); for (4); $\delta(\text{CH})$ 5.18(s), $\delta(\text{CH}_2)$ 4.34 (ABq, J_{AB} 2.5 Hz). All signals disappear on addition of CD₃CO₂D.

range² 1620—1650 cm⁻¹ (Table). It is interesting that compound (**3**; X = Cl, R¹ = Me, R² = Ph) shows two carbonyl bands in solution in CCl₄, whereas the solid (Nujol mull) shows only one band, at 1623 cm⁻¹. Its n.m.r. spectrum (CHCl₃) 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, R¹ = Me, R² = 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.