Unusual Reaction of a Substituted Benzothiazoline with Sulphuryl Chloride: Formation of a 2,2′-(Ethane-1,2-diylidene)bis-1,4-benzothiazine Dye

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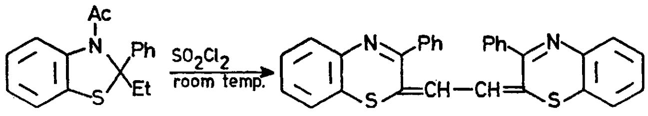
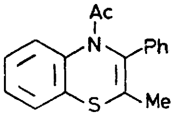
Summary 3-Acetyl-2-ethyl-2-phenylbenzothiazoline (**1**) reacts at room temperature with SO_2Cl_2 to give, in 67% yield, the dye (**2**), by way of the 1,4-benzothiazine (**3**) arising by a new ring expansion reaction.

IN recent years various ring expansion reactions of thiazolidine systems into 1,3-thiazines have been reported in connection with studies on the conversion of penicillins into cephalosporins. However the alternative transformation of thiazolidines into 1,4-thiazines has been very little investigated.[1]

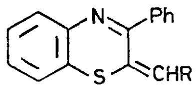
In connection with a study on the transformation of benzothiazoline systems into 1,4-thiazines[2] we have observed that treatment of 3-acetyl-2-ethyl-2-phenylbenzothiazoline (**1**) with *ca.* 2 mol. equiv. of SO_2Cl_2 at room temperature affords the cyanine-like dye (**2**), $C_{30}H_{20}N_2S_2$, m.p. 272—273 °C (from EtOH), in 67% yield. The identification of this compound followed from the ^1H n.m.r. spectrum, δ ($CDCl_3$) 7·9—6·9 (18H, complex m, ArH) and 6·82 (2H, s, 2 × CH), and from the characteristic pH-dependence of the visible spectrum, showing a large reversible bathochromic shift on acidification (λ_{max} 482 → 616 nm), consistent with a cyanine-like chromophore[3] as in (**2**).



(1) (2)



(3)



(4), R = H
(5), R = Cl

The compound (**2**) was identical (i.r., mixed m.p., t.l.c.) with a sample synthesised unambiguously by condensation of 3-phenyl-2*H*-1,4-benzothiazine hydrobromide with an excess of glyoxal hydrate trimer in refluxing acetic acid (59% yield).

The formation of the dye (**2**) probably involves an initial ring expansion of the chlorosulphonium salt of the benzothiazoline (**1**) with S–C(2) cleavage, leading to the benzothiazine (**3**), which could indeed be isolated in 28% yield on treatment of (**1**) with 1 mol. equiv. of SO_2Cl_2. Compound (**3**) reacts with SO_2Cl_2 under the same conditions to give the dye (**2**) presumably by way of the 2-methylenebenzothiazine (**4**) arising from (**3**) by deacetylation promoted by chlorination at C(2).

Evidence supporting the intermediacy of (**4**) in the reaction was provided by the isolation of a chlorine containing derivative, $C_{15}H_{10}NSCl$, identified as (**5**) on the basis of its spectral properties.

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[1] For reviews, see: H. C. van der Plas, 'Ring Transformation of Heterocycles,' Vol. 1, Academic Press, 1974, Ch. 3, p. E3; J. G. Gleason in 'Organic Compounds of Sulphur, Selenium and Tellurium,' Vol. 3, Specialist Periodical Reports, Senior Reporter D. H. Reid, The Chemical Society, London, 1974, Ch. 4.

[2] F. Chioccara, R. A. Nicolaus, E. Novellino, and G. Prota, *Chimica e Industria*, 1976, **57**, 392.

[3] F. Chioccara, G. Prota, and R. H. Thomson, *Tetrahedron*, 1976, **32**, 1407.