

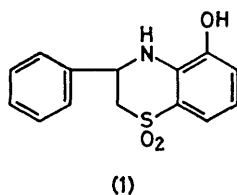
A Novel Synthesis of 1,2,5-Benzoxathiazepines

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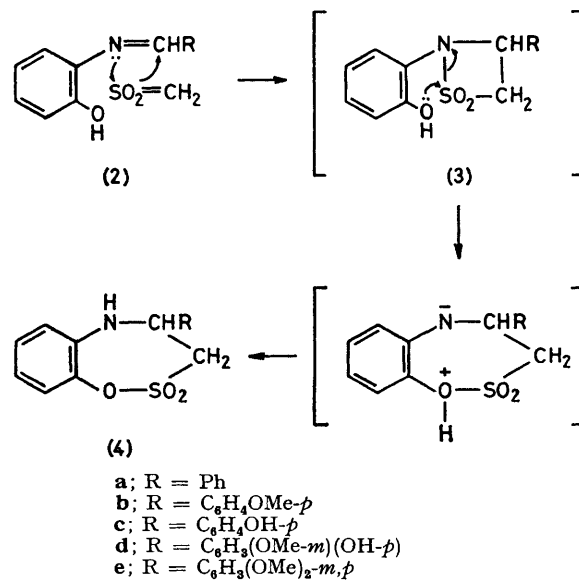
Summary 1,2,5-Benzoxathiazepines have been synthesized through a novel rearrangement reaction of the unstable cycloadducts of sulphene ($\text{H}_2\text{C}=\text{SO}_2$) with substituted *N*-benzylidene-2-hydroxyanilines.

THE reaction of diphenylsulphene ($\text{Ph}_2\text{C}=\text{SO}_2$)† with *N*-benzylideneaniline gives a four membered cyclic compound,¹ but a similar reaction between sulphene ($\text{H}_2\text{C}=\text{SO}_2$) and *N*-benzylideneaniline results in the formation of 1,4-benzothiazine, through a novel rearrangement of the 1,2-cycloadduct.² Addition of $\text{H}_2\text{C}=\text{SO}_2$ to some substituted *N*-benzylideneanilines has also been reported.^{2,3} The present communication describes a new type of rearrangement that occurs during addition of $\text{H}_2\text{C}=\text{SO}_2$ to *N*-benzylidene-2-hydroxyanilines (**2a**–**e**).



Addition of $\text{H}_2\text{C}=\text{SO}_2$, generated *in situ* from methanesulphonyl chloride and triethylamine, to (**2a**) gives a crystalline compound in *ca.* 60% yield, having m.p. 160 °C and an elemental analysis in agreement with the expected 1:1 adduct (**1**) or (**3**). However, spectral studies ruled out structures (**1**) and (**3**) and the product was instead found (mixed melting point) to be identical with 4,5-dihydro-4-phenyl-3*H*-1,2,5-benzoxathiazepine 2,2-dioxide (**4a**), synthesized by an alternative route.⁴

The addition of $\text{H}_2\text{C}=\text{SO}_2$ to (**2**) and the subsequent rearrangement are summarized in the Scheme. Product (**4**), it is postulated, results from migration of the sulphone group from the aniline-nitrogen atom to the *o*-hydroxyoxygen atom followed by a proton shift; thus the 1,2-



SCHEME

thiazetidine ring rearranges to a 1,2,5-benzoxathiazepine ring.

Similarly the analogous 4-substituted 1,2,5-benzoxathiazepine 2,2-dioxides (**4b**) (m.p. 105 °C), (**4c**) (m.p. 123 °C), (**4d**) (m.p. 82 °C), and (**4e**) (m.p. 198 °C) have been synthesized in yields of *ca.* 50% from the corresponding 2-hydroxyanilines (**2b**–**e**), respectively.

(Received, 10th March 1981; Com. 271.)

† Sulphenes are thione *SS*-dioxides.

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² M. Rai, S. Kumar, K. Krishan, and A. Singh, *Chem. Ind. (London)*, 1979, 26.

³ M. Rai, K. Krishan, and A. Singh, *Indian J. Chem.*, 1977, **15B**, 656.

⁴ W. E. Truce, J. W. Fieldhouse, D. J. Vrencur, J. R. Norrel, R. W. Campbell, and D. G. Brady, *J. Org. Chem.*, 1969, **34**, 3097.