

## Synthesis of some Cyclic Sulphoximides

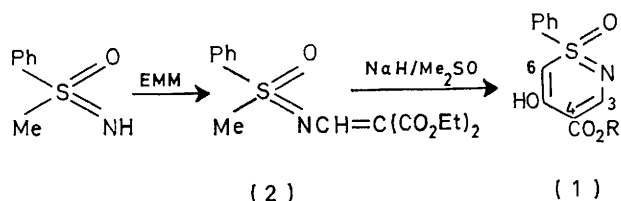
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**Summary** The synthesis of some cyclic sulphoximides is reported, and their n.m.r. data interpreted to show the lack of aromaticity in these systems.

MUCH interest is currently being shown in the possible aromaticity of heterocyclic systems containing hexavalent sulphur.<sup>1-3</sup> We report here on our synthetic studies on cyclic sulphoximides in this category.

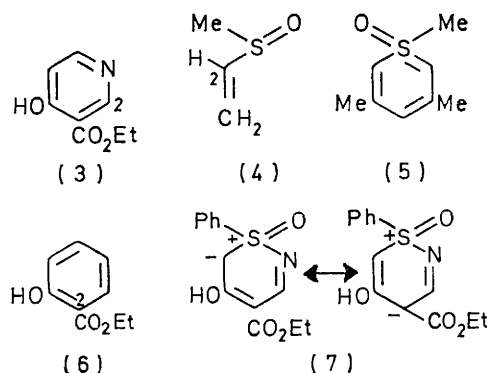
The thiazine oxide (**1**; R=H) was synthesized (Scheme 1) in 43% yield from *S*-methyl-*S*-phenylsulphoximide.<sup>4</sup> Reaction with diethyl ethoxymethylene malonate (EMM) gave the adduct (**2**) as a viscous gum, which on treatment with sodium hydride in dimethyl sulphoxide gave the cyclic ester (**1**; R=Et), m.p. 78–80°. Hydrolysis under mild conditions gave the acid (**1**; R=H). Elemental analysis and spectral data were consistent with the suggested structure.



SCHEME 1.

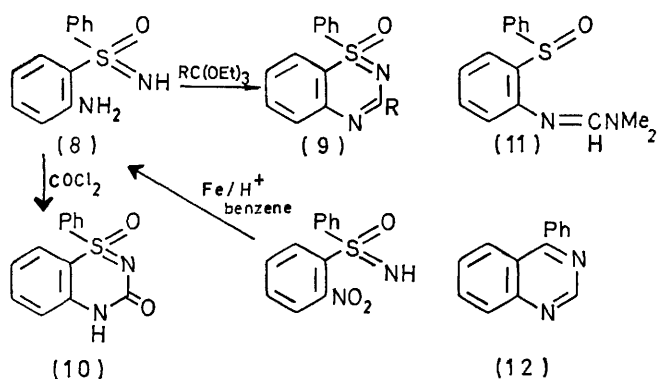
The <sup>1</sup>H n.m.r. spectrum (CDCl<sub>3</sub>) of the ester (**1**; R=Et) exhibited one-proton singlets for 3-H (τ 1.50) and 6-H (τ 4.71) in agreement with the enol ester structure. The 6-H proton exchanges slowly with D<sub>2</sub>O under neutral conditions. Although the position of 3-H is comparable with 2-H (τ 1.80) of the aromatic model (**3**), 6-H is appreciably shielded being well outside the aromatic region, and, in addition,

upfield relative to 2-H (τ 3.57) of the sulphur model (**4**).<sup>5</sup> In the <sup>13</sup>C n.m.r. of the ester the shift of C-3 (37.49 p.p.m. from CS<sub>2</sub>) is close to the shift of C-2 (41.3 p.p.m.) in pyridine, whilst C-6 (113.88 p.p.m.) is comparable with C-2 (109.1



p.p.m.) in the thiabenzene 1-oxide (**5**).<sup>3</sup> C-4 (97.48 p.p.m.) is appreciably shielded relative to C-2 (78.6 p.p.m.) of the aromatic ester (**6**), the low solubility of the pyridine ester (**3**) precluding its use as a model. The high shielding at C-4 and C-6 consequently indicates appreciable carbanionic character of these centres suggesting significant contributions from the ylide structures (**7**), in agreement with the conclusions reached in related series.<sup>2,5</sup>

The benzothiadiazine oxides (**9** and **10**) were prepared from *S*-*o*-aminophenyl-*S*-phenylsulphoximide (**8**) as outlined in Scheme 2. Reaction of the sulphoximide with triethyl orthoacetate gave the cyclic sulphoximide (**9**; R=Me) in 91% yield whose n.m.r. and spectral data were consistent with the suggested structure. Analogous reaction



SCHEME 2.

with triethyl orthoformate gave the sulphoximide (9; R=H), in which the C-3 proton appears in the n.m.r. spectrum (CDCl<sub>3</sub>) at  $\tau$  1.90. This value compares with the shift of the amidine proton in the non-aromatic model (11) which, although not unambiguously determined, lies in the range ( $\tau$  2.5–2.8) similar to values reported for similar amidines,<sup>6</sup> and is considerably upfield from the value for the corresponding proton ( $\tau$  0.65) of the quinazoline (12).

Cyclisation of the *o*-aminosulphoximide (8) with phosgene under mild conditions gave the benzothiadiazinone oxide (10) in 54.5% yield. The spectral data were consistent with the suggested structure and, in particular, the band at 1650 cm<sup>-1</sup> in its i.r. spectrum was consistent with the presence of the urea function in the amide form. Satisfactory analytical data were obtained for all the compounds mentioned.

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