Pummerer-type Reaction of 2-Benzylidene-2,3-dihydro-5-methylbenzo[*b*]-thiophen-3-one 1-Oxide

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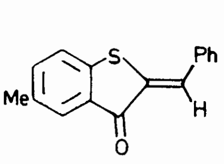
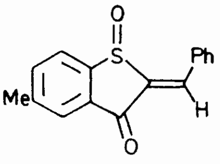
Summary The 2-benzylidene-2,3-dihydro-5-methylbenzothiophenone 1-oxide (**2**) on reaction with methanol or ethanol in the presence of mineral acids afforded $\alpha\beta$-dialkoxy derivatives of 2-benzylidene-2,3-dihydro-5-methylbenzothiophenone; an additive Pummerer-type mechanism for this reaction is suggested.

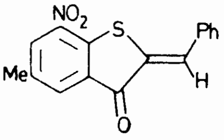
IN a study on the oxidation of *trans*-2-benzylidene-2,3-dihydrobenzo[*b*]thiophen-3-ones we observed an unexpected reaction of the *S*-oxide derivatives of these compounds, related to the recently described additive Pummerer rearrangement.[1] Compound (**1**), on reaction with aqueous nitric acid (65%), yielded the oxide derivative (**2**) (53%), a nitro-derivative (4%) tentatively assigned structure (**3**), and when the products were separated by crystallisation from methanol, the dimethoxy-derivative (**4**) (m.p. 109—110 °C; 2%).† That the *S*-oxide (**2**) may have been an intermediate in the formation of the unexpected dimethoxy-product is supported by the isolation of the same compound (18%) on successive treatment of (**2**) with nitric acid and methanol.



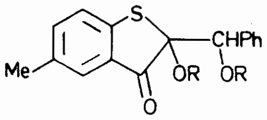
(1)



(2)

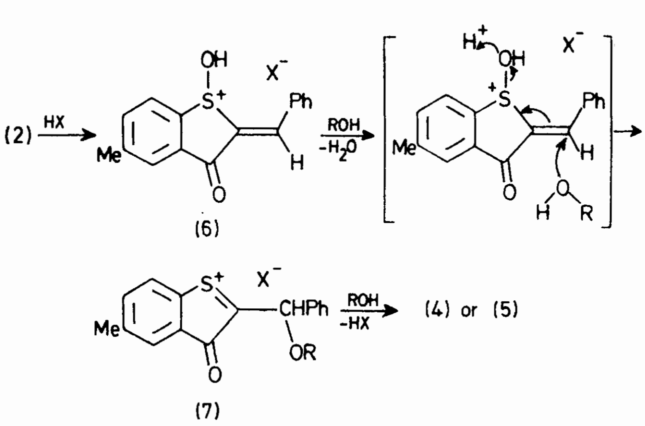


(3)



(4) R = Me
(5) R = Et

A solution of the *S*-oxide (**2**) in methanol was then treated (room temperature; 23 h) with hydrochloric acid (32%) and gave a mixture of the diastereoisomers of the dimethoxy-derivative (**4**) (m.p. 109—110 °C; 59% and m.p. 134—135 °C; 25%). The *S*-oxide (**2**), on reaction with ethanol and hydrochloric acid, yielded the diethoxy-derivative (**5**) (m.p. 94 °C); a second stereoisomer was not isolated in this case. The products of these reactions were identified by satisfactory analytical and spectral data. The configuration of the products is being studied.



R = Me or Et; X = NO_3 or Cl.
SCHEME

A possible pathway for the formation of the dialkoxy-compounds (**4**) and (**5**) from the *S*-oxide (**2**) is outlined in the Scheme. *S*-oxides are known to be weakly basic and may form salts, such as (**6**) with strong acids. The nitric acid salts, R_2SOHNO_3 (R = Me or Et), of dimethyl and diethyl sulphoxides have been prepared.[2] The reaction (Scheme) may be considered a Pummerer reaction‡ in which sulphur-stabilised carbonium ions $(-\mathrm{S}-\overset{+}{\mathrm{C}}\mathrm{H}- \rightleftharpoons -\overset{+}{\mathrm{S}}{=}\mathrm{CH}-)$ such as (**7**) have been suggested[3,4] as intermediates.

The reaction described here is related to the recently reported additive Pummerer rearrangements of methyl cyclopentylidene(phenylsulphinyl)acetate[1] and of 1,4-thiazine 1-oxide derivatives[5] and suggests that this type of reaction of vinyl sulphoxides may have wider applicability.

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† Water was first added to the reaction mixture and the collected products were thoroughly washed with water; presumably some of salt (**6**) must still have been present. However, this point requires further investigation.

‡ According to the definition of that reaction proposed by Johnson and Phillips (ref. 3), namely, 'reactions involving the reduction of a sulphonium sulphur with concomitant oxidation of the α-carbon.'

[1] H. Kosugi, H. Uda, and S. Yamagiwa, *J.C.S. Chem. Comm.*, 1976, 71.
[2] E. H. Rodd, 'Chemistry of Carbon Compounds,' Elsevier, London, 1951, vol. IA, p. 351.
[3] C. R. Johnson and W. G. Phillips, *J. Amer. Chem. Soc.*, 1969, **91**, 682.
[4] W. E. Parham and L. D. Edwards, *J. Org. Chem.*, 1968, **33**, 4150; and references cited therein, and in ref. 3.
[5] J. Kitchin and R. J. Stoodley, *J.C.S. Chem. Comm.*, 1972, 959.