Stevens Rearrangement of a Potentially Aromatic Thiophenium Ylide: Formation of 10-Methoxycarbonyl-10*H*-benzo[3,4]cyclopenta[1,2-*b*]thiopyran-9-one

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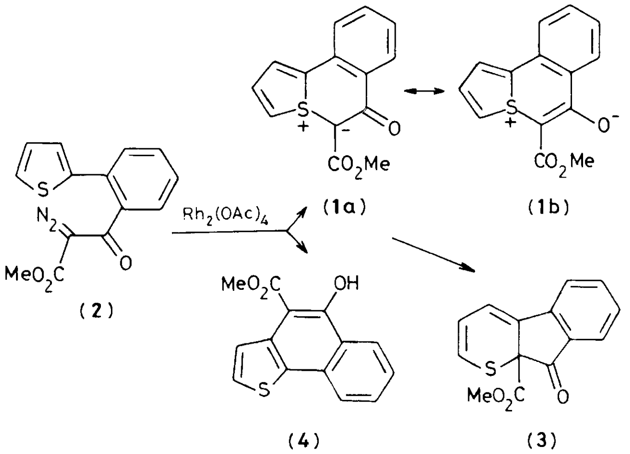
The title compound (**3**) has been obtained by rhodium(II) catalysed decomposition and cyclization of methoxycarbonyl[2-(2′-thienyl)benzoyl]diazomethane (**2**) followed by spontaneous Stevens rearrangement of the initially formed sulphur ylide (**1**).

Only a few carbenes are known to react with thiophenes to give sulphur ylides.[1,2] We have generated a thienyl substituted carbene to achieve an *intra*-molecular attack on the sulphur atom to produce the cyclic ylide (**1a**). This novel heterocycle could show aromatic properties as indicated by the 14 π-electron resonance structure (**1b**). The only previous report of a ring closure reaction at a thiophenic sulphur atom appeared some years ago when a tetrahydrothiopyrano-[1,2-*a*]benzothiophenium salt was described.[3]

The key step in the present work is the rhodium acetate catalysed decomposition and cyclization of the diazo compound (**2**). When this reaction was conducted in benzene solution at room temperature, yellow needles (68% yield; m.p. 133—135 °C) were obtained from diethyl ether after flash chromatography. N.m.r. (^{1}H and ^{13}C), i.r., and mass spectral data suggested, and *X*-ray diffraction analysis unambiguously proved, the structure to be 10-methoxycarbonyl-10*H*-benzo[3,4]cyclopenta[1,2-*b*]thiopyran-9-one (**3**).† This unexpected product is explained by a Stevens rearrangement of the ylide (**1**), indicating a less than anticipated importance of the resonance structure (**1b**).



A minor component (25% yield; m.p. 109—112 °C) was also isolated after flash chromatography and crystallization from methanol. This product was identified by spectroscopic means to be the naphthothiophene (**4**). Formally this could arise from a carbene insertion into the C–H bond in the thiophenic 3-position followed by tautomerization to the fully aromatic (**4**). However, we do not exclude the possibility of a primary formation of a cyclopropathiophene from a carbene attack on

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† All compounds gave satisfactory elemental analyses, and were adequately identified by i.r., ^{1}H and ^{13}C n.m.r., and mass spectral analyses. The synthesis of (**2**) will be described elsewhere. Also a full report of the *X*-ray work will be published elsewhere.

the 2,3-bond in the thiophene ring followed by a direct aromatization to (**4**).‡

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‡ Work on the corresponding compound without the methoxycarbonyl group will be published elsewhere.

References

1 R. J. Gillespie, J. Murray-Rust, R. Murray-Rust, and A. E. A. Porter, *J. Chem. Soc., Chem. Commun.*, 1978, 83.
2 H. Durr, B. Heu, B. Ruge, and G. Scheppers, *J. Chem. Soc., Chem. Commun.*, 1972, 1257.
3 J. A. Cotruvo and I. Degani, *J. Chem. Soc., Chem. Commun.*, 1971, 436.