On the Mechanism of the Catalysed and Uncatalysed Thermolysis of 2,5-Dichlorothiophenium Bismethoxycarbonylmethylide: X-Ray Crystal and Molecular Structure of Methyl 5-Chloro-2-methoxythieno-[3,2-b]furan-3-carboxylate

By ROGER J. GILLESPIE, JUDITH MURRAY-RUST, PETER MURRAY-RUST, and ALEXANDER E. A. PORTER*

(Chemistry Department, University of Stirling, Stirling FK9 4LA, Scotland)

Summary Thermolysis of 2,5-dichlorothiophenium bis-methoxycarbonylmethylide in the absence of transition metal catalysts leads to a novel eliminative rearrangement resulting in the formation of methyl 5-chloro-2-methoxy-thieno[3,2-b]furan-3-carboxylate (4), the structure of which has been confirmed by an X-ray crystal structure determination.

SINCE our initial observation[1] that rhodium(II) carboxylates catalyse the addition of diazomalonic esters to a number of thiophen derivatives to yield stable thiophenium ylides, we have been carrying out a systematic investigation of the general chemistry of this novel class of compounds.

The observation[2] that thiophenium bismethoxycarbonyl-methylide (1; R = H) rearranges to dimethyl 2-thienyl-malonate (2) has prompted us to investigate the possibility of directing the rearrangement of (1; R = Cl) to yield the corresponding dimethyl 3-thienylmalonate (3; R = Cl), since reductive cleavage of the carbon–chlorine bonds would furnish dimethyl 3-thienylmalonate (3; R = H) which is an important intermediate in the production of the semisyn-thetic β-lactam antibiotic ticarcillin.

When heated in the presence of copper or rhodium(II) catalysts, (1; R = Cl) undergoes cleavage of the ylide carbon–sulphur bond resulting in the formation of carbenoid intermediates which have been trapped with olefins and activated aromatic substrates to yield the corresponding cyclopropanes[3] and aryl malonates[4] in good to excellent yields.

(1)   (2)   (3)
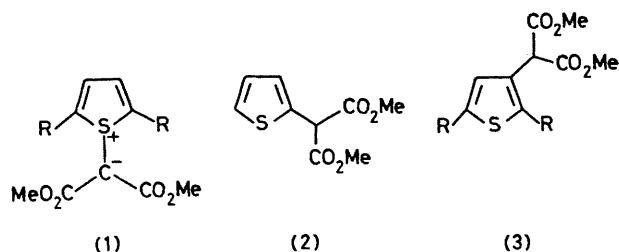
Our initial attempts to carry out thermolysis of (1; R = Cl) in the absence of metal catalysts were thwarted by the fact that minute quantities of the rhodium(II) acetate catalyst are occluded when (1; R = Cl) precipitates during its synthesis and even a very low concentration of the catalyst is sufficient to ensure that the carbenoid mechanism operates during subsequent reactions. However, the last traces of catalyst may be removed by several recrystallisa-tions from acetonitrile.

Thermolysis of the purified ylide (1; R = Cl) in the absence of transition metal catalysts results in a complex mixture of products, but by careful choice of reaction conditions† one major product, m.p. 131—131·5 °C, is formed in ca. 35% yield. Microanalytical and mass spectral data indicated a molecular formula of $C_9H_7ClO_4S$ corresponding to the loss of HCl from the original ylide. The ^1H n.m.r. spectrum showed peaks at τ 3·15 (1H, s), 5·80 (3H, s), and 6·15 (3H, s). These data are consistent

with the structure (4) and crystallographic confirmation was sought.

Crystal data: (4), triclinic, space group $P\bar{1}$, $a = 7\cdot28(1)$, $b = 9\cdot01(1)$, $c = 8\cdot62(1)$ Å, $\alpha = 85\cdot56(1)$, $\beta = 113\cdot54(3)$, $\gamma = 99\cdot57(3)°$; $U = 511\cdot9$ Å^3, $Z = 2$, $F(000) = 252$, μ (Mo-K_α) = $5\cdot00$ cm^{-1}. The structure‡ was solved by the heavy atom method from data collected to $2\theta_{max} = 45°$ on a Stoe 2-circle diffractometer. All atoms except hydrogen were refined anisotropically and for 883 reflections with $I > 3\sigma(I)$, $R = 5\cdot0\%$. The molecule (Figure) is essentially planar with bond lengths in the thiophen ring being comparable with those of thiophen itself.[5]
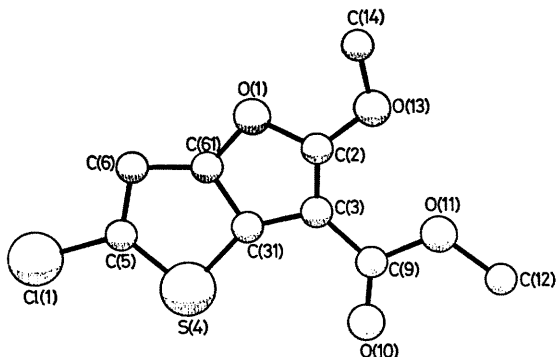

FIGURE. The molecule of methyl 5-chloro-2-methoxythieno-[3,2-*b*]furan-3-carboxylate (4). Bond lengths are (e.s.d.'s *ca.* 0·007 Å): S(4)–C(5), 1·738; S(4)–C(31), 1·728; C(3)–C(31), 1·443; C(2)–C(3), 1·361; O(1)–C(2), 1·367; O(1)–C(61), 1·388; C(6)–C(61), 1·430; C(5)–C(6), 1·430; and C(31)–C(61), 1·352 Å.

When the ylide (1; R = Cl) is heated in anisole in the presence of Cu(acac)$_2$ (Hacac = acetylacetone), conditions under which carbenoids are known to be involved, malonation of the anisole occurs.[3] In the absence of catalyst, no malonation of the anisole occurs indicating that bismethoxycarbonyl carbene is not an intermediate in the reaction. The probable mechanism for the formation of (4) (Scheme) involves the intramolecular[2] transfer of the malonate substituent from sulphur to C-2 of the thiophen ring followed by ring closure and elimination of HCl.

(4)
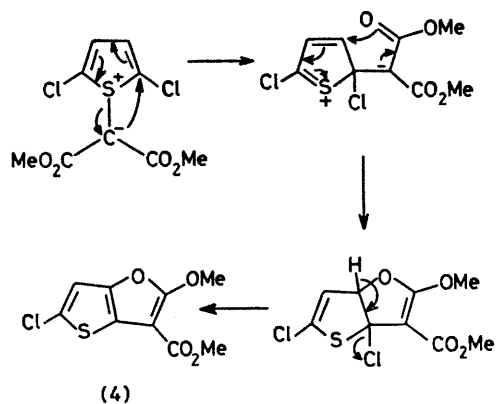
SCHEME

These observations are particularly significant and indicate that cleavage of the ylide carbon–sulphur bond is not a favourable process in the absence of metal catalysts. The role of the metal is not simply to stabilise carbenes generated by the thermal cleavage of the ylide, but must be involved from the outset in the decomposition of the ylide. Although at present no clear-cut mechanistic interpretation of these results is available, it seems probable that the ylide becomes co-ordinated to the Cu(acac)$_2$ and that the co-ordinated ylide undergoes direct decomposition to the carbenoid and dichlorothiophen. Thus the behaviour of the ylide (1; R = Cl) is distinctly different from that of diazoalkanes, diazoketones, and diazoesters[6] which generate carbenes on thermolysis in the absence of metal catalysts and carbenoids on thermolysis in the presence of metal catalysts.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] R. J. Gillespie, J. Murray-Rust, P. Murray-Rust, and A. E. A. Porter, *J.C.S. Chem. Comm.*, 1978, 83.
[2] R. J. Gillespie, A. E. A. Porter, and W. E. Willmott, *J.C.S. Chem. Comm.*, 1978, 85.
[3] J. Cuffe, R. J. Gillespie, and A. E. A. Porter, *J.C.S. Chem. Comm.*, 1978, 641.
[4] R. J. Gillespie and A. E. A. Porter, *J.C.S. Chem. Comm.*, 1979, 50.
[5] W. R. Harshbarger and S. H. Bauer, *Acta Cryst.*, 1970, **B36**, 1010.
[6] W. Kirmse, 'Carbene Chemistry,' 2nd edn., Academic Press, New York, 1971.