

## Thermally Induced Rearrangement of Thiopheniobis(alkoxycarbonyl)methanides. A Theoretical MNDO SCF-MO Study

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The thermal rearrangements of thiopheniobis(hydroxycarbonyl)methanides to give *inter alia* 2*H*-thiopyrans, 2- and 3-substituted thiophenes, and 2,3-cyclopropanated thiophenes have been investigated theoretically using the MNDO SCF-MO method. These calculations indicate that a [1,2]-shift of the bis(hydroxycarbonyl)methanide group from the sulphur to an adjacent carbon atom can occur to form a dipolar intermediate (3). This intermediate is predicted to be the common precursor to all the products observed experimentally in this reaction. In addition, several novel products resulting from the rearrangement of (3) are predicted to be of sufficiently low energy to be capable of detection.

We have described previously<sup>1</sup> how the thermolysis of substituted thiopheniobis(alkoxycarbonyl)methanides (1; R = R' = CO<sub>2</sub>alkyl) yields a range of products according to the experimental conditions and the type of substituent present. Relatively mild thermolysis of (1) gives the 2*H*-thiopyran (5)<sup>2</sup> as the initial kinetic product, whereas higher temperatures result in the formation of the corresponding 2-(2-thienyl)malonates (4)<sup>3</sup> as the thermodynamic product. Variation of the group R also results in the formation of 2,3-cyclopropanated thiophenes<sup>4</sup> (7) and of 3-substituted thiophenes<sup>5</sup> (9). These reactions are additionally known to be regiospecific with respect to the ring substituents in (1).<sup>1</sup>

The rearrangement of (1) can proceed *via* a complex series of pathways (Figure 1). To establish the approximate characteristics of this potential surface, the heats of formation of the various isomers and some of the transition states interconnecting them (Figure 1, R = R' = CO<sub>2</sub>H) were calculated using the

MNDO SCF-MO procedure.<sup>6</sup> This method has recently been reparametrised for sulphur, and has been shown to reproduce reasonably accurately the geometries and energies of a range of sulphur systems. Our preliminary studies at the MNDO level indicated that use of the model group R = H instead of R = CO<sub>2</sub>H was not satisfactory, particularly for some of the dipolar species involved. Accordingly, the entire surface was studied using R = CO<sub>2</sub>H to represent the ester groups. The size of the resulting system and the lack of symmetry in most of the species precluded any systematic study using an *ab initio* SCF-MO procedure.

The most intriguing problem concerns the nature of the species represented by (2). It could be a genuine intermediate in the reaction, providing a pivot for the interconversion of the three compounds (1), (3), and (5). Alternatively it could represent one of three possible transition states for [1,2]-migration in which no cleavage or formation at the bonds

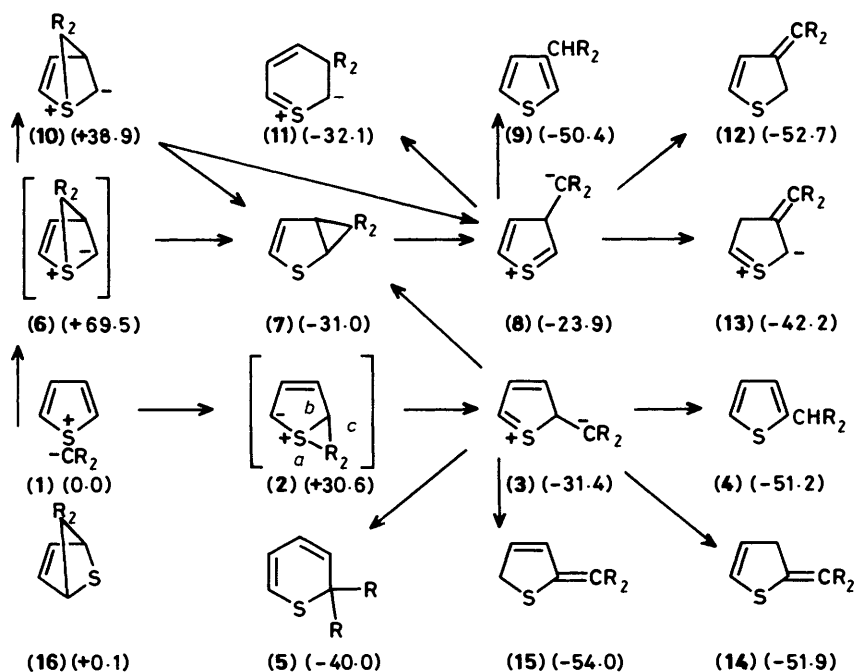
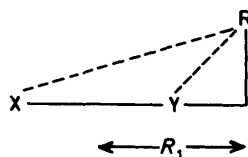


Figure 1. Scheme showing the possible reaction pathways for the rearrangement of (1; R = CO<sub>2</sub>H). Calculated MNDO heats of formation relative to (1) are shown in parentheses, in kcal mol<sup>-1</sup>

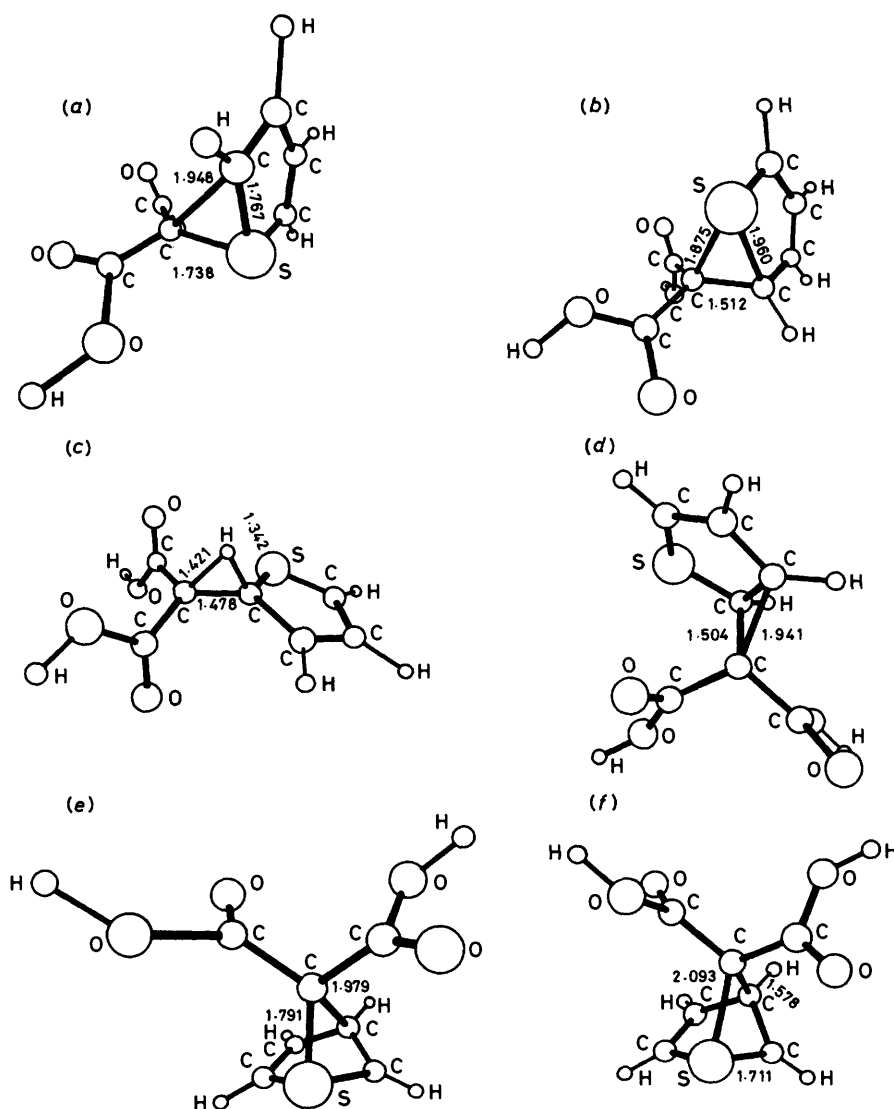
labelled *b*, *a*, or *c*, respectively, corresponds to interconversion of the pairs of species (1) and (3), (1) and (5), or (3) and (5). A minimum energy reaction path calculation using a reaction co-ordinate defined in Figure 2 resulted in the location of *one* stationary point, corresponding to an energy maximum (2). No energy minima other than (1), (3), and (5) could be located by this means on the MNDO potential surface. The calculated barrier is 30.6 kcal mol<sup>-1</sup>, somewhat higher than might be expected for a purely thermal reaction occurring at



**Figure 2.** Reaction co-ordinate definition for studying a [1,2]-migration of group R from Y to X.  $R_1$  Represents the distance between the mid point of the X-Y bond and the perpendicular from R

temperatures of *ca.* 370 K. This could be a result of the minimal *s/p* basis set employed in the MNDO method,<sup>6</sup> but the approximate consistency of this barrier with the observed experimental conditions suggests that this value is not grossly in error. The structure of (2) reveals only one significantly weak bond, corresponding to formation/cleavage of bond *c* [Figure 3(a)]. The transition state for a conventional [1,2]-shift might be expected to have two weak bonds, one forming and the other cleaving, which indicates that (2) resembles more closely the transition state for the formation of a genuine bicyclic intermediate from (1). Our failure to locate such an intermediate suggests it must lie in a very shallow well, or that the reaction co-ordinate defined in Figure 2 is inappropriate.

Subsequent cleavage of bond *a* as the reaction path proceeds would result in the formation of (3), whereas cleavage of bond *b* would result in the formation of (5). Since both of these processes would occur *after* the transition state is passed, classical transition state theory cannot predict which would occur. The simple trajectory calculation employing the reaction co-ordinate defined above suggests that the minimum energy pathway corresponds to cleavage of bond *a* rather than bond *b*,



**Figure 3.** Calculated MNDO transition state structures for the interconversion of (a) (1) and (3), (b) (3) and (5), (c) (3) and (4), (d) (3) and (7), (e) (1) and (10), and (f) calculated structure of the intermediate (10). Bond lengths are shown in Å

resulting in the formation of (3) rather than (5). This real system is surprisingly closely related to a hypothetical potential energy surface discussed by Carpenter<sup>7</sup> in which two reactants and two products are linked by a common intermediate. It was indeed shown for such a system that the product distribution need not always be that predicted by transition-state theory.

We were able to characterise a second transition state directly connecting (3) and (5) [Figure 3(b)] with a calculated activation energy relative to (3) of 32.4 kcal mol<sup>-1</sup>, but were unable to locate any stationary point directly connecting (1) and (5). The experimental isolation at relatively low temperatures of (5) rather than (4) suggests that if (3) is indeed the common precursor to both products, the barrier to the formation of (4) must be higher than that for (5). To form (4) requires a [1,2]-hydrogen shift, and formally at least, such a shift would be a four-electron process, and would be thermally forbidden as a pericyclic reaction. The MNDO transition state corresponding to such a [1,2]-hydrogen migration [Figure 3(c)] corresponded to a barrier of 39.5 kcal mol<sup>-1</sup> relative to (3) for such a shift. This is indeed higher than that for the formation of (5), and its value tends to support the interpretation of this shift as a forbidden pericyclic process. An alternative to the formally forbidden process would be a thermally allowed [1,5]-hydrogen shift to give *e.g.* (14), the calculated energy of which suggests that it represents quite a viable product. In solution it is also quite probable that the hydrogen shift is a result of prototropic equilibria catalysed by traces of acid or base.

The species (3) can rearrange in several other ways. Thus ring closure to give the cyclopropane derivative (7) is calculated to proceed with a relatively low activation energy [15.9 kcal mol<sup>-1</sup> with respect to (3); Figure 3(d)]; a lower barrier than was obtained for rearrangement to give (4) or (5). This is commensurate with a significant degree of biradical character calculated for (3) using the MNDO procedure ( $\langle S^2 \rangle = 1.2$ ),<sup>8</sup> the reaction corresponding to closure of this biradical. However, for R = CO<sub>2</sub>H at least, (7) would not represent the thermodynamic product, since it is calculated to be significantly less stable than either (4) or (5) (Figure 1), and it therefore corresponds to an initially formed kinetic product. The first such product that is actually detected experimentally is, in fact, (5), which implies that (3) and (7) must be in equilibrium. In turn, (7) can re-open to give another dipolar or biradical species (8) isomeric with (3), again with a relatively small barrier [20.0 kcal mol<sup>-1</sup> with respect to (7)]. Species (8) would therefore also be in equilibrium with (3), but since it is calculated to be 7.5 kcal mol<sup>-1</sup> higher in energy, no significant yield of products arising from this species would be expected, at least for the specific substituents R = CO<sub>2</sub>H. If the substituents did affect the relative stabilities of (3) and (8), such a route would indeed provide a pathway for the formation of 3-substituted thiophene products such as (9).<sup>5</sup> The dipolar character of several of the intermediates in Figure 1 [*i.e.* (3), (8), (11), and (13)] and the varying degrees of conjugation possible provide a rationale for the sensitivity of this reaction to the substituents present, both on the ring and in the nature of R. It is known that when R = R' = H<sup>4</sup> or when R = H, R' = CO<sub>2</sub>Et,<sup>1</sup> formation of the 2,3-cyclopropanated thiophene (7) occurs, presumably reflecting the higher stability of (7) compared to dipolar species such as (3) or (8). The high regioselectivity shown in the formation of *e.g.* (5) suggests that substituent effects may also control the relative stability of derivatives of (3) substituted on the ring.<sup>1</sup>

There is also another pathway that might result in the formation of (7), involving the direct [1,3]-migration of the bis(alkoxycarbonyl)methylene group. The calculated potential energy surface for this route is different in one respect from formally analogous [1,2]-migration discussed above. Thus a transition state (6) was located [Figure 3(e)], leading to an intermediate bicyclic species (10) [Figure 3(f)], which could in

turn give either (7) or (8) directly. Species (6) and (2) are formally analogous, whereas (10) represents the intermediate on the reaction pathway that we were unable to locate for the [1,2]-shift. The calculated energy of (6) compares unfavourably with the route involving intermediacy of the species (3), (7), and (8) (Figure 1), and a species such as (10) seems unlikely to be involved in the rearrangement process.

Several hitherto uncharacterised species are also predicted to be low energy systems. Thus the novel dipolar heterocycle (11) would be formed by electrocyclic ring opening of (7) and its calculated energy (Figure 1) suggests that if substituted with an electron withdrawing group at the 2-position it may be capable of isolation. Species (3) or (8) are also capable of rearranging directly to a number of other, as yet unobserved, products. The bicyclic species (16) is effectively precluded because of its very high calculated energy, but products such as (12)—(15) are calculated to be low in energy and seem probable candidates for isolation. Indeed furan analogues of (14) are known.<sup>9</sup> The dipolar species (13) is also interesting since it too may be stabilised by electron-withdrawing groups at the 2-position.

*Computational Procedure.*—MNDO SCF-MO calculations<sup>6</sup> were carried out using the AMPAC program system<sup>10</sup> and the recently reported parameter set for sulphur.<sup>6</sup> The basis set used consisted of an *sp* set throughout, no *d*-functions being included. All geometrical parameters were fully optimised with respect to the calculated energy. Since several of the species involved could be envisaged as having biradical or open shell wavefunctions, all the calculations were carried out using the spin-unrestricted UHF procedure, which has been shown to lead to qualitatively correct bond homolysis behaviour leading to biradicals.<sup>8</sup> Transition states corresponding to [1,2]-migrations were located for three reactions, the conversion of (1) to the intermediate (3), and the breakdown of (3) to give either the thiopyran (5) or the 2-substituted malonate product (2). The one-dimensional reaction co-ordinate system shown in Figure 2 was used. Here, *R*<sub>1</sub> represents horizontal translation of the group involved in the [1,2]-migration. In each case, a maximum in the energy as a function of *R*<sub>1</sub> was obtained. The calculated structures at the energy maxima were refined by minimising the sum of the squared scalar gradients,<sup>11</sup> and characterised as genuine transition states by showing that the calculated force constant matrix had only one negative root of the correct form.<sup>12</sup> In the case of the reaction (1) → (3) in particular, no evidence was obtained from the reaction path of any intermediate, suggesting that at this level of theory at least, (2) is a genuine transition state.

## Acknowledgements

We thank the University of London for a generous allocation of time on the FPS-164 system at Imperial College Computer Centre.

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*Received 19th February 1987; Paper 7/311*