Thermal Rearrangement of Thiophenium Bismethoxycarbonylmethylides: a Novel Synthesis of Thiophene-2-malonic Esters[1]

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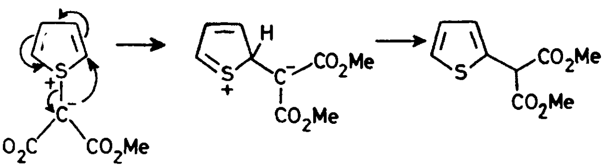
Summary Thermolysis of thiophenium bismethoxycarbonylmethylide results in a ready rearrangement to dimethyl thiophene-2-malonate.

We have shown[2] that rhodium(II) acetate catalyses the addition of dimethyl diazomalonate to thiophen to yield thiophenium ylides (**1**), and that the process is truly catalytic in that the catalyst may be recycled without appreciable diminution in yields of the ylide.† Ylides prepared by this method are obtained in high yields and require no purification, since after simple filtration the products are pure by all analytical criteria‡ and are thus ideal intermediates for further structural transformation.



(1) (2)

The observation that copper(I) salts catalyse the formation of dimethyl thiophene-2-malonate (**2**) (albeit in low yield) during the reaction of dimethyl diazomalonate with thiophen suggested to us that this product might arise by the rearrangement of the ylide (**1**) formed *in situ* during the reaction. To test this possibility (**1**) was heated at reflux in thiophen solution (the conditions under which the copper-catalysed addition of dimethyl diazomalonate to thiophen is carried out) and after 2 h the ylide had completely decomposed to one major product (70%), subsequently identified as the ester (**2**). Minor by-products of this reaction were shown to be polymers of bismethoxycarbonylcarbene (**3**).

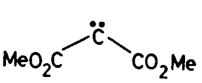
The ester (**2**) also results when dimethyl diazomalonate is added to a refluxing solution of the rhodium catalyst in thiophen during 2 h and this reaction has the distinct advantage of offering a one-step synthesis of (**2**) from thiophen.

Thermal rearrangement of the thiophenium ylides appears to be general. For example, the ylide (**4**) on refluxing in 2-methylthiophen for 3 h rearranges smoothly to the malonate (**5**) in 95% yield.

Two main mechanistic pathways appear likely for this reaction. The ylide may undergo an intramolecular rearrangement (Scheme), or decomposition of the ylide may result in the formation of the carbene (**3**) which then functions as an electrophile to give the expected 2-substitution product.

Formation of the malonate (**2**) from (**1**), and (**5**) from (**4**) appears to be independent of solvent, with yields of *ca.* 70 and 90% respectively. When cyclohexene, vinyl acetate, dimethyl acetylenedicarboxylate, or ethyl cinnamate are used as solvents there is no evidence of cyclopropanated products in the reaction mixture suggesting that the carbene (**3**) is not an intermediate. This is supported by the absence of the dimer (**6**) in any of the reaction mixtures.

The failure to trap the carbene (**3**) is indicative of an intramolecular rearrangement and an attempt has been made to confirm this by cross-over experiments. Rearrangement of (**1**) in 2-methylthiophen gives exclusively (**2**) with no trace of the cross-over product (**5**). Similarly rearrangement of (**4**) in thiophen gives exclusively (**5**) with no evidence for the formation of (**2**) clearly supporting the intramolecularity of the rearrangement.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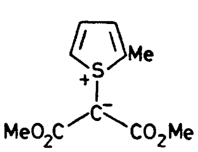
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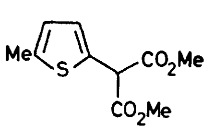
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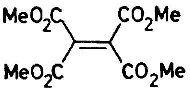
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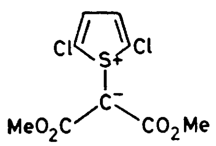
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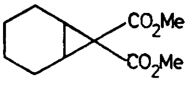
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(9)

2,5-Disubstituted thiophenium bismethoxycarbonyl methylides are also thermally unstable but the reaction appears to be more complex than with simple derivatives such as (**4**). The methylide (**7**) on thermolysis in dichlorothiophen produces a complex mixture of products which have defied identification owing to decomposition on attempted purification by preparative layer chromatography; however, when heated in thiophen, (**7**) gave a quantitative yield of the malonate (**2**).

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† In a typical reaction the catalyst (5.5 mg) was dissolved in thiophen (10 ml) and dimethyl diazomalonate (1.58 g, 10 mmol) was added over 1 h. The reaction was complete (i.r.) after 24 h, and the product (2 g, 95%) was obtained by filtration. Removal of the ylide by filtration followed by a further addition of dimethyl diazomalonate to the filtrate has proven an adequate method of recycling the catalyst. After five successive runs under these conditions, the catalytic activity is retained.

‡ All new compounds exhibit satisfactory spectral and microanalytical properties.

When heated in cyclohexene, (**7**) gave both the cyclopropanated derivative (**8**) and the carbene insertion product (**9**) confirming the dissociation into dichlorothiophen and the carbene (**3**). This is probably a consequence of the steric bulk of the two chlorine atoms coupled with a weakening of the carbon–sulphur bond due to the inductive electron withdrawal of the two chlorine atoms. The high yield of (**2**) from the dichloro ylide (**7**) and thiophen may be due to the operation of an alternative pathway (*viz.* electrophilic substitution) when the carbene is being generated under conditions not conducive to ylide formation.

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[1] R. J. Gillespie, A. E. A. Porter, and W. E. Willmott, B. P. Appl., 22625/77.

[2] R. J. Gillespie, J. Murray-Rust, P. Murray-Rust, and A. E. A. Porter, preceding communication.