

Rhodium(II)-catalysed Addition of Dimethyl Diazomalonate to Thiophen: a Simple Synthesis of Thiophenium Bismethoxycarbonylmethylides¹ and Crystal and Molecular Structure of the Unsubstituted Methylide

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Summary Rhodium(II) acetate-catalysed addition of dimethyl diazomalonate to thiophen and its derivatives results in the formation of stable crystalline thiophenium ylides; the structure of thiophenium bismethoxycarbonylmethylide has been determined by *X*-ray analysis.

THE thermal² and photochemical³ addition of diazoacetic esters to π -excessive heterocycles such as thiophen, furan, and pyrrole⁴ to give the cyclopropanated products (**1**, X=S or O, Y=H), and pyrrole-2-acetic acid are well documented processes. However, no reports on the addition of diazomalonic esters to these systems have appeared.†

We considered that the 2-thiabicyclo[3.1.0]hexene-dicarboxylate (**1**; X=S, Y=CO₂Me) might serve as a useful starting point³ for the synthesis of 2- and 3-substituted thiophen derivatives (see following communication). Initial attempts to induce thiophen to react with dimethyl diazomalonate using conventional catalysts such as copper(I) chloride, silver acetate, and iodo(triphenyl phosphite)-copper(I)⁵ proved impractically slow; the characteristic diazo i.r. band at 2100 cm⁻¹ was still present after the mixture had been heated under reflux for 8 days. However, from the reaction mixture it was possible to isolate dimethyl thiophen-2-malonate in *ca.* 36% yield along with the carbene dimer (**2**).

† In a recent review (*Accounts. Chem. Res.*, 1977, **10**, 179) W. Ando has reported the generation of thiophenium bismethoxycarbonylmethylide by a photochemical route.

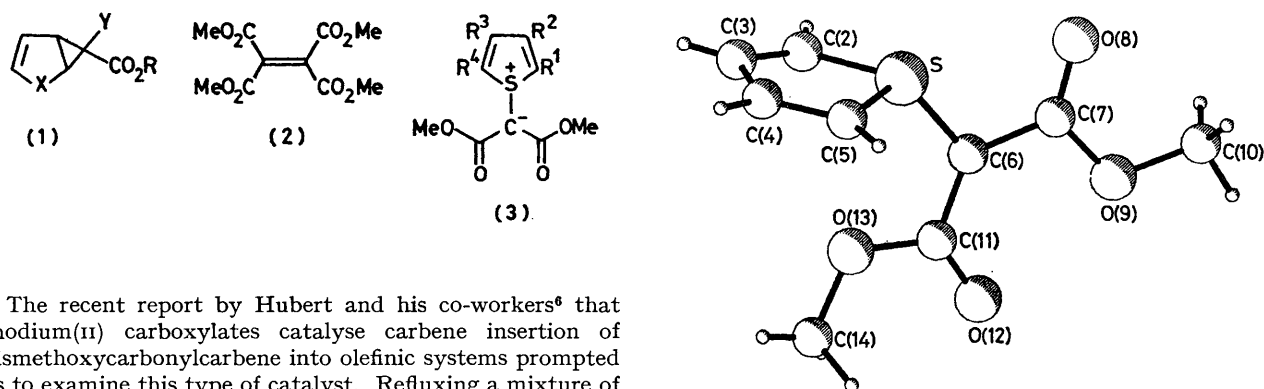


FIGURE. The structure of the ylide (**3**; $R^1=R^2=R^3=R^4=H$). Bond lengths (Å): S-C(2) 1.745(7); S-C(5) 1.743(4); S-C(6) 1.711(4); C(2)-C(3) 1.326(6); C(3)-C(4) 1.439(10); C(4)-C(5) 1.320(8); C(6)-C(7) 1.441(6); C(6)-C(11) 1.431(6). Bond angles (degrees): C(2)-S-C(5) 92.2(3); C(2)-S-C(6) 116.8(2); C(5)-S-C(6) 114.7(2).

The recent report by Hubert and his co-workers⁶ that rhodium(II) carboxylates catalyse carbene insertion of bismethoxycarbonylcarbene into olefinic systems prompted us to examine this type of catalyst. Refluxing a mixture of thiophen and dimethyl diazomalonate in the presence of rhodium(II) acetate resulted in a rapid evolution of nitrogen and within 15 min the diazo i.r. band was no longer present, confirming an extremely rapid reaction of the diazo ester, but under these conditions the major product was the dimer (**2**) formed in quantitative yield. When a mixture of the dimethyl diazomalonate and thiophen was stirred at room temperature in the presence of the rhodium catalyst, the reaction followed a different course with the slow (18 h) formation of a colourless precipitate, m.p. 145–146 °C (from MeCN), ν_{\max} (CHCl₃) 3120, 3000, 1650 (br), 1435, 1330, and 1230 (br) cm⁻¹; τ (CDCl₃) 2.9 (4H, AA'BB' m) and 6.35 (6H, s). Microanalysis and mass spectral data supported a molecular formula of C₉H₁₀SO₄ indicating that the product was the ylide (**3**; $R^1=R^2=R^3=R^4=H$) and a crystal structure determination was undertaken to confirm the structure.

Crystals of (**3**; $R^1=R^2=R^3=R^4=H$) are monoclinic, space group *C2/c*, $a = 19.56(2)$, $b = 9.28(1)$, $c = 14.08(1)$ Å, $\beta = 51.70(1)^\circ$, $U = 2004.3$ Å³, $Z = 8$, $F(000) = 1328$, $\mu(\text{Mo-K}\alpha) = 2.6$ cm⁻¹. The structure was solved by direct methods from data collected to $2\theta_{\max} = 55^\circ$ on a Stoe 2-circle diffractometer. All atoms[†] except hydrogen were refined anisotropically and for 1427 independent reflections with $I > 3\sigma(I)$, $R = 5.6\%$.

The molecule (Figure) has an approximate mirror plane with the sulphur atom pyramidal as expected, and the ylide bond is significantly shorter by (0.035 Å) than the C-S bonds in the thiophen ring. There is greater localisation of double bonds than in thiophen itself⁷ (C-S = 1.718, C _{α} -C _{β} = 1.369, C _{α} -C _{β'} = 1.443 Å) and this probably reflects the shift of electron density from the ring to the malonate group. There is no obvious structural clue to the exceptional stability of the malonate derivative.

The reaction of diazomalonate esters with several other thiophen derivatives has been examined (Table), and when substituents with +*I* or +*M* effects are present then ylides

are formed in high yields. When substituents with -*M* effects are present then no reaction occurs as typified by the failure of 2-acetyl-, 2-cyano- and 2-formyl-thiophen to undergo reaction.

TABLE ^a

Thiophen substituents	R ¹	R ²	R ³	R ⁴	% Yield
Unsubstituted	H	H	H	H	95
2,5-Cl ₂	Cl	H	H	Cl	100
2-HOCH ₂	HOCH ₂	H	H	H	92
2-Br, 3-Me	Br	Me	H	H	86
2-Me	Me	H	H	H	90
2-Br	Br	H	H	H	95

^a In reactions of 2- and 3-acetyl-, 2-cyano-, and 2-formyl-thiophen, the ylide (**3**) was not obtained.

It is of interest to note that other systems which are capable of stabilising ylide structures do not form thiophenium ylides; ethyl diazoacetate, ethyl diazoacetate, and diazoacetophenone under the same conditions give rise to the products (**1**; X=S, Y=COMe), (**1**; X=S, Y=CO₂Et), and (**1**; X=S, Y=Ph) respectively, with no evidence of intermediate ylides, suggesting the necessity of fairly stringent electronic demands for stabilisation of the ylide structure in this system.

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[†] 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.

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