2,5-Dichlorothiophenium Bismethoxycarbonylmethylide: a Bismethoxycarbonylcarbene Equivalent

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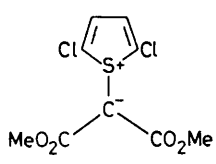
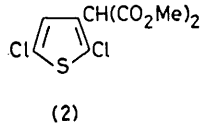
Summary 2,5-Dichlorothiophenium bismethoxycarbonylmethylide, a stable crystalline solid, functions as an excellent bismethoxycarbonylcarbene equivalent.

IN an earlier report[1] we have described the rhodium(II) acetate-catalysed addition of diazomalonic esters to thiophen derivatives[2] and a novel intramolecular rearrangement of the resulting ylides to yield derivatives of thiophen-2-malonic esters.

In an attempt to direct the rearrangement to produce 3-substituted thiophen derivatives we have examined the rearrangement of 2,5-dichlorothiophenium bismethoxycarbonyl methylide (**1**). Under normal rearrangement conditions[3] low yields of dimethyl 2,5-dichlorothiophen-3-malonate (**2**) were produced along with a number of by-products, suggesting an alternative reaction pathway for the decomposition of (**1**), possibly by a dissociative mechanism.



(1)



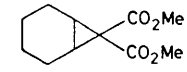
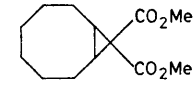
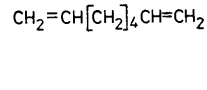
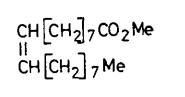
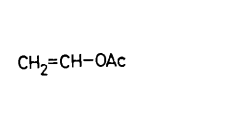
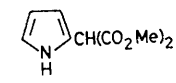
(2)

When the reaction was carried out in cyclohexene in the absence of rhodium(II) acetate, the reaction was sluggish but when the rhodium catalyst, or preferably copper(II) acetylacetonate was present, a high yield of the cyclopropanated product was obtained, suggesting the intermediacy of bismethoxycarbonylcarbene or more probably a metal carbenoid species.

In view of the current interest in the applications of bismethoxycarbonylcarbene in synthetic methodology[4,5] we decided to examine the possible use of the dichloro-ylide (**1**) as a carbene precursor and our preliminary results are shown in the Table.

We believe that the ylide (**1**) offers a number of distinct advantages as a source of bismethoxycarbonylcarbene. It is a stable crystalline compound which may be stored without special precautions at ambient temperature.† In all the examples examined yields are comparable with, and in many cases superior to the use of dimethyldiazomalonate as a carbene source, and reaction times are invariably shorter. However, the main advantage is clearly the ease with which the reaction may be carried out, particularly on a small scale. When diazomalonic esters are used, reaction conditions appear to be crucial in determining the yield of products, with catalyst concentrations

TABLE[a]

Reactant	Product	Yield (%)	Temp (°C)	Time (h)
		66[b]	Reflux	16
		86	120	0·5
		83[c]	120	1·5
		60	110	0·5
		81	75	1·1
		73[d]	85	2·5
MeCO$_2$H	MeCO$_2$CH(CO$_2$Me)$_2$	98·5	100	4

[a] In all cases the quoted yields are of isolated products. The reaction of cyclo-octene is typical. A mixture of the ylide (1·00 g) and Cu(acac)$_2$ (10 mg) in cyclo-octene (10 ml) was stirred at 120 °C. After 30 min t.l.c. (SiO_2,$CHCl_3$–MeOH, 97:3) indicated that the reaction was complete. Evaporation of the excess cyclo-octene followed by passage through a short silica column gave 9,9-bismethoxycarbonyl-bicyclo[6.1.0]-nonane, 0·73 g (86%), m.p. 69—70 °C (lit.[6] 68—69 °C). [b] B. W. Peace and D. S. Wulfmann, *Synthesis*, 1973, 137. [c] A small yield (*ca.* 2%) of the dicyclopropanated product was also formed in this reaction. [d] The yield and the time taken for this reaction to go to completion is particularly sensitive to many factors such as batch size, catalyst concentration, and temperature.

† Samples of the ylide (**1**) have been stored at ambient temperature for more than one year without any sign of deterioration.

and addition rate[6] of the diazo ester playing important roles.

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