The Rearrangement of Isothiochroman Sulphonium Ylides *via* a Thermal Ylide Exchange Reaction

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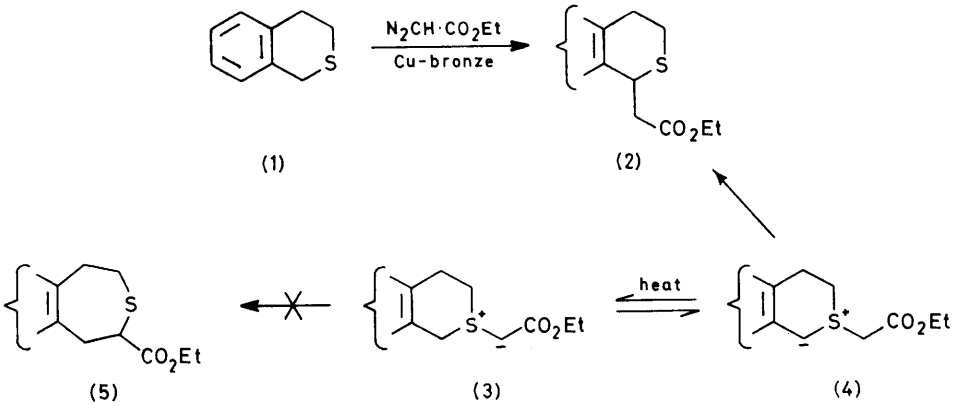
The copper-bronze-catalysed decomposition of ethyl diazoacetate in isothiochroman (1) yields mainly ethyl isothiochroman-1-ylacetate (2). The formation of the ester (2) is rationalized in terms of a thermal ylide exchange reaction of the unstable sulphonium ylide initially formed, prior to a Stevens-type rearrangement. Thermal decomposition of the stable bis(ethoxycarbonyl)(isothiochroman-2-io)methanide (6) yields diethyl isothiochroman-1-ylmalonate (8), in support of the above mechanism.

RECENT interest in the rearrangement of sulphonium ylides [1] prompts us to report evidence for thermal ylide exchange reactions in cyclic sulphonium ylides [2] and confirmation of their susceptibility to thermal cleavage of the dipolar sulphur–carbon bond to give the products of Stevens-type rearrangements.[3]

The copper-bronze-catalysed thermal decomposition of ethyl diazoacetate in isothiochroman (1), in benzene at 80 °C for 14 h, gave ethyl isothiochroman-1-ylacetate (2) as the only isolated product (30%) and some polymeric material.[4] For the formation of the unusual C–H insertion product (2) we suggest that the unstable ylide intermediate (3) is transformed into the endocyclic ylide (4) by a thermal ylide exchange reaction. In the ensuing Stevens-type rearrangement, ejection of $RO_2C{\cdot}CH^-$ from (4) and its subsequent attack on the resulting cation, or coupling of the radical pair formed



[1] For a discussion, see B. M. Trost and L. S. Melvin, jun., 'Sulfur Ylides, Emerging Synthetic Intermediates,' Academic Press, New York, 1975, pp. 14 *et seq.*

[2] *Cf.* W. E. Parham and R. Koncos, *J. Amer. Chem. Soc.*, 1961, **83**, 4034; W. Ando, S. Kondo, K. Nakayama, K. Ichibori, H. Kohoda, H. Yamato, I. Imai, S. Nakaido, and T. Migita, *ibid.*, 1969, **91**, 2786, and references cited therein.

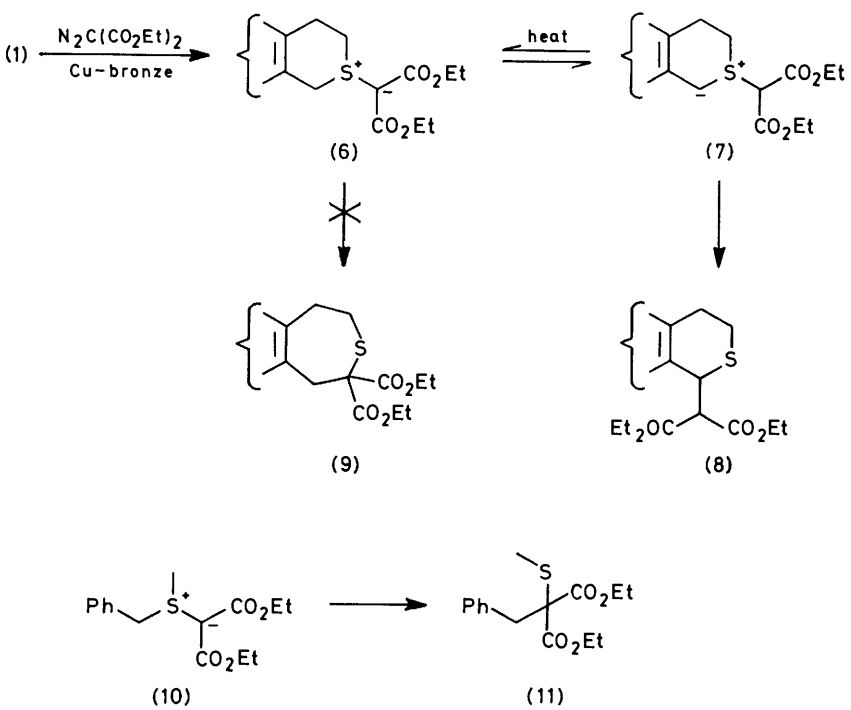
[3] T. S. Stevens, *Progr. Org. Chem.*, 1968, **7**, 48; W. Ando, H. Fujii, T. Takeuchi, H. Higuchi, Y. Saiki, and T. Migita, *Tetrahedron Letters*, 1973, 2117.

[4] *Cf.* W. Ando, T. Yagihara, S. Kondo, K. Nakayama, H. Yamato, S. Nakaido, and T. Migita, *J. Org. Chem.*, 1971, **36**, 1732.

by homolytic cleavage of (4),* would account for the formation of the ester (2).

This mechanism is supported by the formation of the analogous Stevens rearrangement product (8) in the thermolysis of the stable ylide (6) which was obtained in 70% yield by the copper-bronze-catalysed decomposition of diethyl diazomalonate in isothiochroman (1).† Heating the ylide (6) in a sealed tube for 4 h at 150 °C gave dimethyl isothiochroman-1-ylmalonate (8) as the only isolated product in 60% yield.

In the above reactions the ring-expansion products



(5) and (9), which could arise by Stevens rearrangement of the ylides (3) and (6), respectively, were not detected.

In contrast with our results, Ando [7] has reported the formation of benzylmalonate (11) as the only product of the thermolysis of the acyclic benzylmethylsulphonium ylide (10). This difference in behaviour can be explained if in the thermal ylide exchange the preference for endocyclic ylides (4) and (7) is a consequence of a steric advantage in the proton transfer.

In order to confirm their structures, the products (2) and (8) were prepared by an alternative sequence. Isothiochroman (1) was treated with *N*-bromosuccinimide in carbon tetrachloride to give 1-bromoisothiochroman,[8] which on treatment with diethyl sodiomalonate gave (8) as a single product in 30% yield. The ethyl isothiochroman-1-ylacetate (2) was obtained from (treatment with base.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage app I.r. spectra were obtained with a Beckmann IR5 s photometer. ^1H N.m.r. spectra were recorded JEOL IMN-C-60 HL spectrometer (solutions in tetrachloride with internal tetramethylsilane as sta Microanalyses were performed by the analytical lab of Carlo Erba, Milano.

Isothiochroman was prepared by cyclization of (thio)acetic acid, followed by Wolff–Kishner redu Ethyl diazoacetate was prepared as described.[10] diazomalonate was prepared by treatment of a solu diethyl malonate and tosyl azide with triethyla Column chromatography was performed with Merc gel (0.063—0.200 mm particle size).

Reaction of Isothiochroman (1) *with Ethyl Diazoac* To a stirred suspension of isothiochroman (1) (12 mol) and copper-bronze (0.490 g) in benzene (20 ml) at 80 °C under nitrogen, ethyl diazoacetate (6 g, 0.05 dissolved in benzene (20 ml) was added over 3 h solution was then refluxed for 14 h and cooled, filtere evaporated, and the excess of isothiochroman (6 distilled off at low pressure. The oily residue (8 chromatographed on a silica gel column. Elutio 99 : 1 benzene–ethyl acetate gave *ethyl isothiochroma*

* A CIDNP effect has recently been observed in the Stevens rearrangement and so, at least in part, this must also involve diradical intermediates. For a discussion on this topic see ref. 5.

† Many stable bis(carboethoxy) sulphonium ylides have been prepared in recent years by the catalysed decomposition of diazobisalkoxy compounds in sulphides. For a review see ref. 6.

[5] A. R. Lepley and G. L. Closs in ' Chemically Induced Magnetic Polarization,' ed. A. R. Lepley and G. L. Closs, Wiley, New York, 1973, pp. 323 *et seq.*

[6] W. Ando, *Internat. J. Sulfur Chem.* (*B*), 1972, 188.

[7] W. Ando, T. Yagihara, S. Tozune, I. Imai, J. Suz Toyama, S. Nakaido, and T. Migita, *J. Org. Chem.*, 1972, 3

[8] R. Pellicciari, M. Curini, and P. Ceccherelli, *Il Farm Sci.*, 1975, 837.

[9] K. Kiang and F. G. Mann, *J. Chem. Soc.*, 1951, 1909.

[10] N. E. Searle, *Org. Synth.*, 1956, **36**, 25.

[11] B. W. Peace, F. Carman, and D. S. Wulfman, *Sy* 1971, 658.

acetate (2) (2.8 g, 30%) (Found: C, 66.15; H, 6.85; S, 13.6. $C_{13}H_{16}O_2S$ requires C, 66.1; H, 6.85; S, 13.55%); $\nu_{max.}$ (CCl_4) 1 730 cm^{-1} (C=O); δ ($CDCl_3$) 1.25 (3 H, t, $CO_2{\cdot}CH_2{\cdot}CH_3$), 2.7—3.1 (6 H, m, 3 × CH_2), 4.14 (2 H, q, $CO_2{\cdot}CH_2{\cdot}CH_3$), 4.37 (1 H, t, *J* 8 Hz, benzylic), and 7.1 (4 H, s, aromatic).

Bis(ethoxycarbonyl)(isothiochroman-2-io)methanide (6).—To a solution of isothiochroman (1) (6 g, 0.04 mol) in dry benzene (7 ml), freshly prepared copper-bronze (2 g) was added. To this mixture, kept under nitrogen with stirring at 80 °C, a solution of diethyl diazomalonate (4 g, 0.012 5 mol) in dry benzene (10 ml) was added dropwise over 3 h, and the mixture was kept at 80 °C for 24 h. The solvent was removed under vacuum, the excess of isothiochroman (4 g) distilled off, and the residue (6 g) purified by column chromatography on silica gel. Elution with 90 : 10 benzene–ethyl acetate and recrystallization of the solid obtained (4.8 g) from diethyl ether gave the *ylide* (6) (4.3 g, 70%), m.p. 106—108° (Found: C, 62.25; H, 6.5; S, 10.3. $C_{16}H_{20}O_4S$ requires C, 62.3; H, 6.55; S, 10.4%); $\nu_{max.}$ ($CHCl_3$) 1 663 and 1 619 cm^{-1} (C=O); δ ($CDCl_3$) 1.29 (6 H, t, $CO_2{\cdot}CH_2{\cdot}CH_3$), 2.2—3.55 (4 H, m, 2 × CH_2), 3.13 (1 H, d, *J* 12 Hz, H-1), 4.29 (4 H, q, $CO_2{\cdot}CH_2{\cdot}CH_3$), 4.95 (1 H, d, *J* 12 Hz, H-1), and 6.5—6.95 (4 H, m, aromatic).

Thermolysis of the Ylide (6).—The ylide (6) (1 g) was sealed in a Pyrex tube without degassing and heated at 140 °C for 3 h. After complete decomposition the mixture was chromatographed on a silica gel column. Elution with benzene gave a solid (0.7 g), crystallization of which from diethyl ether yielded *diethyl isothiochroman-1-ylmalonate* (8) (0.6 g, 60%), m.p. 108—110° (Found: C, 62.7; H, 6.2. $C_{16}H_{20}O_4S$ requires C, 62.3; H, 6.55%); $\nu_{max.}$ ($CHCl_3$) 1 740 cm^{-1} (C=O); δ ($CDCl_3$) 1.02 and 1.32 (each 3 H, t, $CO_2{\cdot}CH_2{\cdot}CH_3$), 2.6—3.2 (4 H, m, 2 × CH_2), 3.8 (1 H, d, *J* 11 Hz, α-H), 3.92 and 4.25 (each 2 H, q, $CO_2{\cdot}CH_2{\cdot}CH_3$), 4.25 (1 H, d, *J* 11 Hz, benzylic), and 7 (4 H, s, aromatic).

The Malonate (8).—Diethyl malonate (2.8 g, 0.0174 mol) was added dropwise to a suspension of sodium hydride (0.42 g, 0.0174 mol) in anhydrous benzene (35 ml) and the mixture was stirred under nitrogen at room temperature for 3 h. A solution of 1-bromoisothiochroman (4 g, 0.0174 mol) in dry ethanol (35 ml) was added over 45 min with stirring at room temperature. The suspension was refluxed under nitrogen for 6 h, then poured onto ice and extracted with chloroform. The extract was washed with water, dried (Na_2SO_4), and evaporated under vacuum. The oily residue (4.5 g) was purified by chromatography on a silica gel column. Elution with benzene–ethyl acetate (98 : 2) gave unchanged bromoisothiochroman followed by a product (1.3 g, 30%) identical (b.p., i.r., and n.m.r.) with the malonate (8) described above.

The Acetate (2).—To a stirred solution of the malonate (8) (0.2 g, 0.65 × 10^{-4} mol) in ethanol (6 ml), 2.5N-sodium hydroxide (2.8 ml) was added, and the mixture was refluxed for 10 h. The solvent was removed under vacuum, water was added to the residue, and the mixture was extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated to give an oily residue (0.135 g), purified by chromatography on a silica gel column. Elution with benzene–ethyl acetate (95 : 5) gave a product (0.106 g, 75%) identical (b.p., i.r., and n.m.r.) with the acetate (2) described above.

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