## Evidence for the Participation of a Nitrile Group in [2,3] Sigmatropic Rearrangements of Sulphonium Ylides

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Summary The formation of N-methylthiomethylketenimines from the reaction of  $\alpha$ -cyanoalkyl-dimethylsulphonium salts with n-butyl-lithium or triethylamine occurs by way of a [2,3] sigmatropic rearrangement of intermediate ylides.

ALLVLSULPHONIUM ALKYLIDES undergo a thermal [2,3] sigmatropic rearrangement to generate homoallylic sulphides.<sup>1</sup> Carbonyl groups are also able to participate in this electrocyclic reaction yielding enol ethers.<sup>1,2</sup> A sigmatropic process with the participation of nitrile groups to generate ketenimines is not yet known. However, replacement of a double bond by a triple bond does not appear to prohibit reaction, since prop-2-ynylic sulphonium ylides readily give allenic compounds by a [2,3]sigmatropic rearrangement.<sup>3</sup> We now report reactions which show that cyanosulphonium ylides rearrange to ketenimines.

The sulphides (1a) and (1b) were prepared by sulphenylation of the anion of the corresponding nitriles with dimethyl disulphide.<sup>4</sup> The sulphide (1c) was prepared by sulphenylation with *N*-methylthiosuccinimide.<sup>5</sup> Alkylation of the sulphides (1) was carried out at room temperature, with  $Me_3O^+X^-$  in MeCN, to yield the stable sulphonium salts (2a,  $X = BF_4$ ), m.p. 131 °C (50%); (2b,  $X = BF_4$ ), m.p. 139 °C (20%); and (2c,  $X = PF_6$ ), m.p. 140 °C (30%).

The ylide intermediates (3), which were not isolated, were generated by the reaction of (2) with Bu<sup>n</sup>Li or NEt<sub>3</sub> in tetrahydrofuran at 0 °C. The ylide (3a) gave the ketenimine (4a) [oil, 35%,  $\nu_{max}$  2010 cm<sup>-1</sup> (C=C=N); <sup>1</sup>H n.m.r.  $\delta$  (CDCl<sub>3</sub>) 2·01 (s, Me), 2·16 (s, Me), and 4·50 (s, CH<sub>2</sub>)] and the sulphide (5), a Sommelet Hauser rearranged product [oil, 65%,  $\nu_{max}$  2238 cm<sup>-1</sup> (C=N); <sup>1</sup>H n.m.r.  $\delta$ (CDCl<sub>3</sub>) 1·66 (d, Me), 2·06 (s, Me), 3·72 (CH<sub>2</sub>, ABq, J 13·5 Hz), and 4·38 (q, CH)]. Desulphurisation of (5) with Raney nickel<sup>6</sup> in ethanol yielded the nitrile (6) (70%), identical with an authentic sample prepared by hydrolysis and decarboxylation<sup>7</sup> of methyl 2-*o*-tolyl-2-cyanopropanoate.

The reaction of the salt (2b) with Bu<sup>n</sup>Li or NEt<sub>3</sub> gave the ketenimine (4b) [oil, 25%, spectral data analogous to those for (4a)], and compound (7) [oil, 75%,  $\nu_{max}$  2229 and 2240 cm<sup>-1</sup> (C=N); <sup>1</sup>H n.m.r.  $\delta$  (CDCl<sub>3</sub>) 2·01 (s, Me), 6·14 (d, CH), and 6·30 (d, CH, J 4 Hz)] which arises from an  $E_2$  elimination with (2b)<sup>8</sup> or an intramolecular elimination of the ylide (3b).<sup>9</sup>

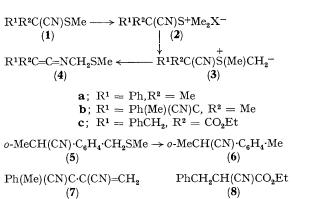
Deprotonation of the salt (2c) with Bu<sup>n</sup>Li gave the cyanoester (8) (20%) and the ketenimine (4c) [oil, 80%, spectral data analogous to those for (4a)]. The ketenimine

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(4c) was also identified by hydration to the amide (9) [m.p. 92 °C,  $v_{max}$  1648 and 1737 (C=O), and 3235 cm<sup>-1</sup> (NH); <sup>1</sup>H n.m.r.  $\delta$  (CDCl<sub>3</sub>) 1·16 (t, Me), 2·05 (s, Me), 3·40 (m, CH<sub>2</sub>-CH), 4.14 (q,  $CH_2$ ), and 4.32 (m,  $NH-CH_2-S$ )]. The most reasonable mechanism for the formation of (8) is via addition of BuLi to the sulphur atom of the sulphonium salt and elimination of anion of the cyanoester (8).8

There is no trace of the corresponding nitrile (10) among the products of rearrangement of (3). These results are in accordance with a [2,3] sigmatropic rearrangement of the ylide intermediates (3) to the ketenimines (4). A simultaneous formation of (4) and (10) would be expected if the rearrangement was a radical process (Stevens' type) or an ionic one.

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R<sup>1</sup>R<sup>2</sup>C(CN)CH<sub>2</sub>SMe PhCH<sub>2</sub>CH(CO<sub>2</sub>Et)CONHCH<sub>2</sub>SMe (9) (10)

<sup>1</sup> For a review of [2,3] signatropic rearrangements of allylsulphonium and allenylsulphonium ylides, see B. M. Trost and L. S. Melvin Jr., 'Sulfur Ylides,' Academic Press, New York, 1975, 108. <sup>2</sup> K. W. Ratts and A. N. Yao, J. Org. Chem., 1968, 33, 70; E. B. Ruiz, Acta Salmenticensia, Ser. Cience, 1958, 2, 64 (Chem. Abs., 1960, 54, 7623); Y. Hayashi and R. Oda, Tetrahedron Letters, 1968, 5381. <sup>3</sup> J. E. Baldwin, R. E. Hackler, and D. P. Kelly, Chem. Comm., 1968, 1083; A. Terada and Y. Kishida, Chem. Pharm. Bull. (Japan),

1970, 18, 991; P. A. Griego, M. Meyers, and R. S. Finkelhor, J. Org. Chem., 1974, 39, 119; G. Pourcelot, L. Veniard, and P. Cadiot, Bull. Soc. Chim. France, 1975, 1275, 1281.

<sup>4</sup> E. Marchand, G. Morel, and A. Foucaud, Synthesis, 1977, in the press.

<sup>5</sup> D. N. Harpp, B. Friedlander, D. Mullins, and S. M. Vines, *Tetrahedron Letters*, 1977, 963. <sup>6</sup> P. G. Gassman and G. Gruetzmacher, *J. Amer. Chem. Soc.*, 1973, 95, 588.

7 R. Delaby, P. Reynaud, and F. Lily, Bull. Soc. chim. France, 1960, 864.

<sup>8</sup> V. Franzen and C. Mertz, Angew. Chem., 1960, 72, 416; Chem. Ber., 1960, 93, 2819; E. J. Corey and W. Oppolzer, J. Amer. Chem. Soc., 1964, 86, 1899.

<sup>9</sup> W. Ando, M. Yamada, E. Matsuzaki, and T. Migita, J. Org. Chem., 1972, 37, 3791.