

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 α -cyanoalkyl-dimethylsulphonium salts with *n*-butyl-lithium or triethylamine occurs by way of a [2,3] sigmatropic rearrangement of intermediate ylides.

(**2a**, X = BF₄), m.p. 131 °C (50%); (**2b**, X = BF₄), m.p. 139 °C (20%); and (**2c**, X = PF₆), m.p. 140 °C (30%).

The ylide intermediates (**3**), which were not isolated, were generated by the reaction of (**2**) with BuⁿLi or NEt₃ in tetrahydrofuran at 0 °C. The ylide (**3a**) gave the ketenimine (**4a**) [oil, 35%, ν_{\max} 2010 cm⁻¹ (C=C=N); ¹H n.m.r. δ (CDCl₃) 2.01 (s, Me), 2.16 (s, Me), and 4.50 (s, CH₂)] and the sulphide (**5**), a Sommelet Hauser rearranged product [oil, 65%, ν_{\max} 2238 cm⁻¹ (C≡N); ¹H n.m.r. δ (CDCl₃) 1.66 (d, Me), 2.06 (s, Me), 3.72 (CH₂, ABq, *J* 13.5 Hz), and 4.38 (q, CH)]. Desulphurisation of (**5**) with Raney nickel⁶ in ethanol yielded the nitrile (**6**) (70%), identical with an authentic sample prepared by hydrolysis and decarboxylation⁷ of methyl 2-*o*-tolyl-2-cyanopropanoate.

The reaction of the salt (**2b**) with BuⁿLi or NEt₃ gave the ketenimine (**4b**) [oil, 25%, spectral data analogous to those for (**4a**)], and compound (**7**) [oil, 75%, ν_{\max} 2229 and 2240 cm⁻¹ (C≡N); ¹H n.m.r. δ (CDCl₃) 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**)⁸ or an intramolecular elimination of the ylide (**3b**)⁹.

Deprotonation of the salt (**2c**) with BuⁿLi gave the cyanoester (**8**) (20%) and the ketenimine (**4c**) [oil, 80%, spectral data analogous to those for (**4a**)]. The ketenimine

ALLYLSULPHONIUM ALKYLIDES undergo a thermal [2,3] sigmatropic rearrangement to generate homoallylic sulphides.¹ Carbonyl groups are also able to participate in this electrocyclic reaction yielding enol ethers.^{1,2} 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.³ 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.⁴ The sulphide (**1c**) was prepared by sulphenylation with *N*-methylthiosuccinimide.⁵ Alkylation of the sulphides (**1**) was carried out at room temperature, with Me₃O⁺X⁻ in MeCN, to yield the stable sulphonium salts

