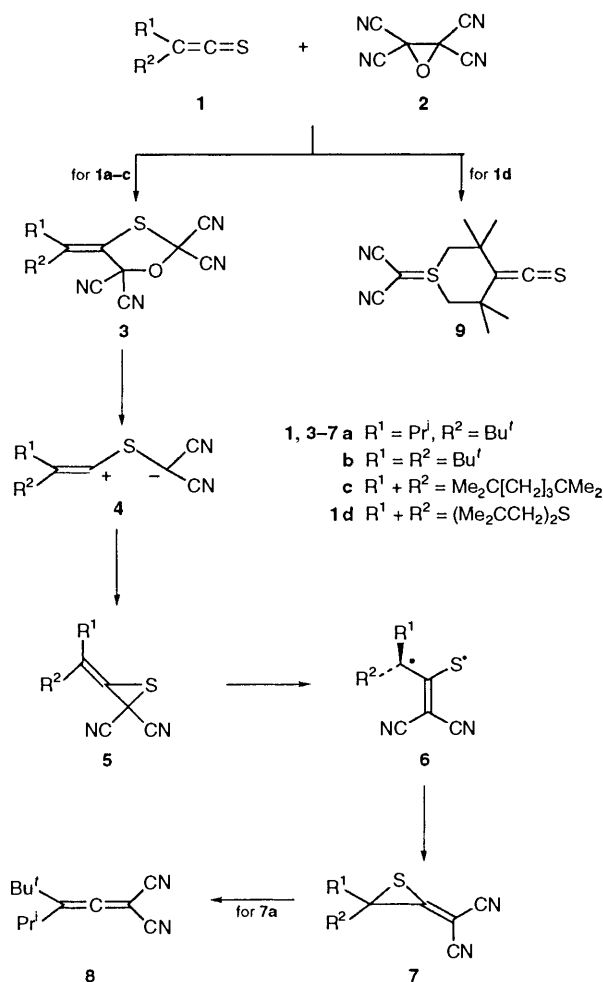


Dicyanomethylenethiiranes from Thioketenes and Tetracyanoethylene Oxide

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Reaction of dialkylthioketenes with tetracyanoethylene oxide yields dicyanomethylenethiiranes in a sequence involving [3 + 2] cycloaddition, cycloreversion and rearrangement. In contrast, a thioketene with a sulfide moiety reacts preferentially on the latter to give the stable sulfur ylide **9**.

Oxiranes with electron-withdrawing substituents are a convenient source of carbonyl ylides and give the corresponding [3 + 2] cycloadducts with a broad range of π electron systems.¹ However, among C=S compounds, this is only true for the reaction of thiono esters with dicyanoethylene oxide,² whereas other thiocarbonyl compounds and oxiranes such as **2** react with olefination of the C=S group to a dicyanomethylene



unit.^{3,4} Insights into the reaction course are provided by the present study on the reaction of thioketenes **1** with oxirane **2**.

On addition of oxirane **2** to purple solutions of thioketenes **1a-c** in tetrahydrofuran (THF) or 1,2-dichloroethane at room temperature or on heating, the reaction mixture was decolourized and, after chromatographic work-up (SiO₂), adducts corresponding to loss of mesoxalodinitrile were isolated in 32–61% yield. This suggests formation of allene episulfides **5** assuming initial formation of heterocycles **3** by [3 + 2] cycloaddition of tetracyanocarbonyl oxide on the C=S moiety of **1**⁵ and a subsequent [3 + 2] cycloreversion⁶ via thiocarbonyl ylide **4**. However, in the IR spectrum of **5** the alkylidene moiety should give rise to a band around 1775 cm⁻¹.⁷ In contrast, the observed absorption at 1610–1630 cm⁻¹ is in accord with a push-pull substituted olefin unit as in the isomeric allene episulfide **7**. In addition, assignment of structure **7** is supported by the magnetic non-equivalence of the cyano groups in the ¹³C NMR spectra.

Similar rearrangements of allene episulfides to the isomers with the bulky substituents on the thiirane ring have been reported for alkyl^{5,8} or silyl substituted derivatives.⁹ Based on a zwitterionic intermediate analogous to **6**, the stabilization of the negative charge by the silyl group (R¹ = SiMe₃) has been invoked as driving-force for the isomerization.⁹ As the cyano groups should have an even stronger electronic effect and do not lead to stabilization of **5** this rationale can be ruled out at least for the present examples. In contrast, we assume a thiatrimethylenemethane intermediate **6** where steric interactions between the bulky groups R¹, R² and the sulfur work against coplanarity, but favour spin-pairing to give **7**.

In addition to products **7**, starting from **1a** 36% of allene **8** was isolated. Thus, by analogy with previous results,²⁻⁴ olefination of the thiocarbonyl group may be the final outcome of the reaction also starting from **1**.

A striking exception is observed in the reaction of thioketene **1d** and **2**. Here, the product showed an IR absorption at 1750 cm⁻¹ which would be compatible with the structure of an unrearranged thiirane **5**.⁷ However, the product was pink indicating the presence of an intact thiocarbonyl unit. In fact, an X-ray structural investigation (Fig. 1) confirmed formation of a sulfur ylide **9** resulting from attack of the electrophilic oxirane **2** on the sulfide moiety in **1d**.¹⁰ Bond distances in the equatorial sulfur ylide moiety¹¹ and in the linear thioketene functionality¹² are in accord with reported values. Interestingly, the sulfur ylide functionality adopts a conformation which bisects the plane of the cyclohexane ring obviously in order to minimize repulsion between the sulfur lone pair and the π -electrons on the ylide carbon.

In summary, isolation of thiiranes **7** provides the missing link to account for olefin formation as observed on addition of epoxides such as **2** to most thiocarbonyl compounds. Reaction of thioketene **1d** on the sulfide moiety demonstrates possible competition by a more nucleophilic sulfur functionality.

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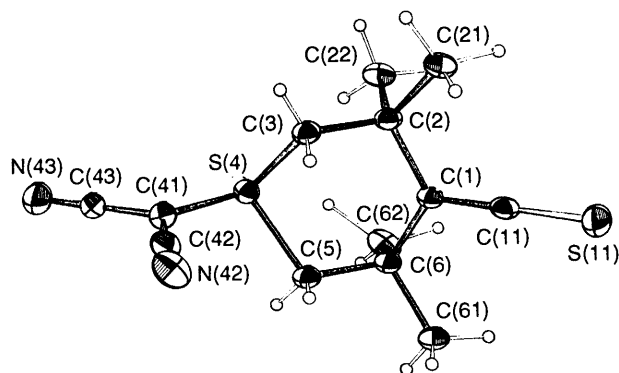


Fig. 1 ORTEP drawing of **9** showing 35% probability ellipsoids. Important bond distances, in pm, are: S(11)–C(11), 154.4; C(1)–C(11), 130.6; S(4)–C(41), 170.8; C(41)–C(42), 141.2; C(41)–C(43), 139.0 (esds 0.4–0.7 pm).

However, the observed chemoselectivity has a parallel in the reaction of **1d** with peracids.¹³

Experimental

Thioketenes **1**¹⁴ and oxirane **2**¹⁵ were obtained according to literature procedures.

Typical Procedure for the Reaction of Thioketenes with Tetracyanoethylene Oxide.—Thioketene **1c** (0.45 g, 2.5 mmol) and tetracyanoethylene oxide (0.36 g, 2.5 mmol) were dissolved in dry diethyl ether (20 cm³) and the mixture was stirred at 20 °C for 14 h. Then the solvent was evaporated and the products separated by chromatography on silica gel using ethyl acetate–light petroleum (1 : 9). First fraction, unreacted **1c** (0.30 g); second fraction, thiirane **7c** (0.40 g, 32%, based on reacted **1c**), m.p. 80–81 °C (Found: C, 68.3; H, 7.4; N, 11.3; S, 13.35. C₁₄H₁₈N₂S requires C, 68.25; H, 7.4; N, 11.4; S, 13.0%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1630; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.86, 1.32 (s, 6 H each) and 1.86 (s, 6 H); $\delta_{\text{C}}(\text{CDCl}_3)$ 74.9, 80.1 (thiirane-C), 111.4, 112.6 (CN) and 178.7 [C=C(CN)₂].

Analogously were prepared: compound **7a**, 40%, m.p. 73–74 °C (Found: C, 65.6; H, 7.5; N, 12.6; S, 14.6. C₁₂H₁₆N₂S requires C, 65.4; H, 7.3; N, 12.7; S, 14.55%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1620; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.15 (s, 9 H), 0.91, 1.06 (d, 3 H each) and 2.96 (sept, 1 H); $\delta_{\text{C}}(\text{CDCl}_3)$ 74.9, 80.8 (ring-C), 111.7, 112.5 (CN) and 178.5 [C=C(CN)₂]; compound **7b**, 61%, m.p. 64–65 °C (Found: C, 66.8; H, 7.7; N, 12.0; S, 12.9. C₁₃H₁₈N₂S requires C, 66.6; H, 7.7; N, 11.95; S, 13.7%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1610; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.24 (s); $\delta_{\text{C}}(\text{CDCl}_3)$ 74.9, 80.6 (ring-C), 111.8, 112.7 (CN) and 178.9 [C=C(CN)₂]; compound **8**, 36%; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1920; compound **9**, 55%; m.p. 154 °C (dec.) (Found: C, 58.9; H, 6.2; N, 10.5; S, 24.0. C₁₃H₁₆N₂S₂ requires C, 59.1; H, 6.1; N, 10.6; S, 24.2%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1750; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.41, 1.59 (s, 6 H each) and 3.18 (s, 4 H); $\delta_{\text{C}}(\text{CDCl}_3)$ 13.7 [S=C(CN)₂] and 116.7 (CN).

Structure Determination of Ylide 9.—Rotating-crystal, Weissenberg and precession photographs gave approximate lattice constants and suggested space group *P2*₁/*n*. Refinement of the lattice constants led to the cell dimensions: *a* = 625.3(1),

b = 2576.8(1), *c* = 878.2(1) pm, β = 91.61° (1), *V* = 1415 × 10⁶ pm³, space group = *P2*₁/*n*, *Z* = 4, *D*_x = 1.24 g cm⁻³; $\mu(\text{Cu-K}\alpha)$ = 31.93 cm⁻¹.

Intensity data were collected on a CAD4-SDP single-crystal diffractometer using Cu-K α radiation in the range 2° < θ < 65° using a graphite monochromator. The final refinement was based on 2080 symmetry-independent reflections with *I* > 3 σ (*I*). The structure was solved by the direct-methods program MULTAN. The E map revealed the position of all the heavy atoms. After the refinement of these positions, the H atoms were found from a difference Fourier synthesis. Convergence was achieved at *R* 0.056 (*R*_w 0.062). Programs and further details of techniques are given in ref. 12. Fractional atomic coordinates, tables of bond lengths and angles as well as of anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.*

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* For details of the CCDC Deposition Scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, 1993, issue 1.

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