Synthesis of Tris(imino)thietans; *X*-Ray Crystal Structure of 2,3-Bis-(t-butylimino)-4-*p*-tolylsulphonyliminothietan

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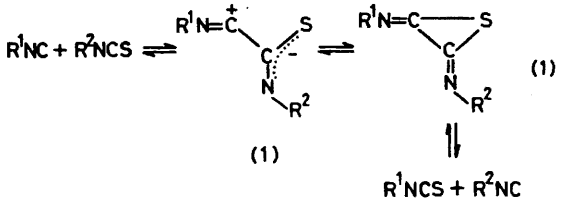
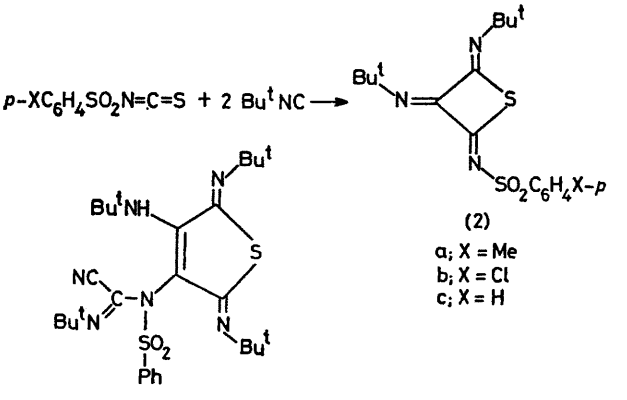
Summary The first examples of tris(imino)thietans (**2**) have been prepared by treatment of arylsulphonyl isothiocyanates with t-butyl isonitrile; the structure of the *NN'*-di-t-butyl-*N''*-*p*-tolylsulphonyl derivative has been determined by *X*-ray crystallography.

EXTERNALLY stabilized 1,3-dipoles of type (**1**) are probably intermediates in the reversible transfer of sulphur from aryl isothiocyanates to aryl isonitriles [equation (1), R^1 and R^2 = aryl].[1] By varying the substituents R^1 and R^2, we were



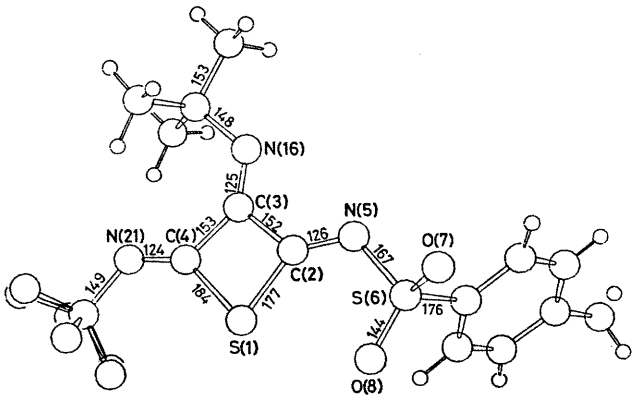
able to trap the dipolar species with a second molecule of isonitrile to yield the title compounds (**2a**—**c**):[2] (**2a**), 60% yield, m.p. 131·5 °C (decomp.) (from Et_2O); (**2b**), 65%, m.p. 140—142 °C (decomp.) (from Et_2O); (**2c**), 61%, m.p. 86—87 °C (from hexane).† Thus, when arylsulphonyl isothiocyanates were treated with **2** equiv. of t-butyl isonitrile in ether at room temperature (1 day), the yellow adducts (**2a** and **b**) crystallized out upon cooling of the mixture. The adduct (**2c**) was isolated by column chromatography on silica gel with ether–n-hexane (50:50) as eluant. This also furnished a side product (6%, m.p. 178 °C, decomp.) which was identified as (**3**) by *X*-ray analysis.



The i.r. spectra (KBr) of (**2a**—**c**) showed characteristic imine stretching absorptions at 1720—1730w, 1660m, and 1600—1610s, br cm^{-1}, while the ^1H n.m.r. spectra indicated the presence of two t-butyl groups (δ 1·40 and 1·50). The

† All compounds gave satisfactory elemental analyses. Yields were not optimized; those for (**2a**) and (**2b**) refer to the recrystallized compounds, while that for (**2c**) is for the compound following column chromatography.

^{13}C n.m.r. spectra ($CDCl_3$), showed ring carbon absorptions at δ 145—146, 162—163, and 176—177 p.p.m. The structure of (**2a**) was determined by *X*-ray analysis, and a drawing of the structure is shown in the Figure, which indicates the stereochemistry about the three imine double bonds.‡ *Crystal data:* $C_{18}H_{25}N_3O_2S_2$, monoclinic, space group $P2_1/n$, $a = 22{\cdot}104(9)$, $b = 8{\cdot}616(3)$, $c = 11{\cdot}038(3)$ Å, $\beta = 100{\cdot}83(3)°$; $Z = 4$. Intensities were determined with a Syntex diffractometer with Mo-K_α radiation; $2\theta_{max} = 42°$. The structure was solved by MULTAN 77[3] and refined with the *X*-RAY 72 system[4] to an *R*-value of 0·049 for 1504 significant reflections. As expected, the nitrogen atoms are nearly coplanar with the thietan ring. The average deviation from the least-squares plane passing through the seven atoms is 0·037 Å.



FIGURE

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] J. H. Boyer and V. T. Ramakrishnan, *J. Org. Chem.*, 1972, **37**, 1360.
[2] For the synthesis of imino-substituted four-membered rings from isonitriles, see B. Zeeh, *Synthesis*, 1969, 65.
[3] P. Main, L. Lessinger, M. M. Woolfson, G. Germain, and J. P. Declercq, 'MULTAN 77, a System of Computer Programmes for the Automatic Solution of Crystal Structures from *X*-ray Diffraction Data,' York and Louvain-la Neuve (Belgium), 1977.
[4] J. M. Stewart, G. J. Kruger, H. L. Ammon, C. Dickinson, and S. R. Hall, '*X*-ray 72 System. Technical Report TR-192, Computer Centre, University of Maryland,' 1972.