Preparation of Sulphenamidines. *X*-Ray Crystal Structure of *N*^{1},*N*^{1}-Dimethyl-*N*^{2}-methylthiobenzamidine

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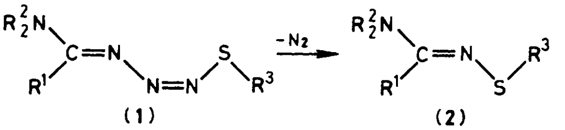
Readily available 3-(α-dialkylaminobenzylidene)-1-alkylthiotriazenes, when stirred in dichloromethane solution with copper(I) cyanide catalyst, give good yields of (*E*)-sulphenamidines (a new class of compounds): the mechanism of this extrusion reaction is discussed and the structure of one of the sulphenamidines has been established.

Previously we reported[1] that *S*-alkyl quaternary salts of *N*,*N*-disubstituted thioamides react with aqueous sodium azide solution at room temperature, giving crystalline products for which we proposed thia(S^{IV})triazole structures while concluding that *X*-ray crystal analysis was necessary for proof. This, when carried out later,[2] showed that, in spite of the mild conditions of formation, rearrangement had occurred, and the products were (1*Z*,3*E*)-3-(α-dialkylaminoalkylidene)-1-alkylthiotriazenes (**1**).

We now report that when the triazene (**1a**) in dichloromethane solution is stirred in an ice bath with copper(I) cyanide as catalyst, rapid evolution of nitrogen occurs, complete in 30 min, giving, in 75% yield, (*E*)-*N*^{1},*N*^{1}-dimethyl-*N*^{2}-methylthiobenzamidine (**2a**) as colourless rods from petroleum, m.p. 95—96 °C; M^+ 194; $\delta(CDCl_3)$ 7.5 (3H, m, ArH, *m*- and *p*-), 7.3 (2H, m, ArH, *o*-), 2.84 (6H, s, NMe_2), and 2.56 (3H, s, SMe); ν_{max}(Nujol) 1560s, 770m, and 710m cm^{-1}; λ_{max} (hexane) 314 nm (ϵ_{max} 2170).

Similarly the triazene (**1b**) gives (**2b**) in 84% yield as colourless rhombs from petroleum, m.p. 84 °C; M^+ 236; $\delta(CDCl_3)$ 7.4 (5H, m, ArH), 3.65 (4H, m, 2 × CH_2O), 3.25 (4H, m, 2 × CH_2N), and 2.53 (3H, s, SMe); ν_{max} (Nujol) 1560s, 1260s, 1110s, and 710m cm^{-1}; λ_{max} (hexane) 310 nm (ϵ_{max} 2900).



a; R^1 = Ph, R^2 = R^3 = Me
b; R^1 = Ph, NR^2 = 4-morpholino, R^3 = Me

The compound, with ethanolic picric acid at room temperature, gave, quantitatively, the picrate of morpholinobenzylideneamine as yellow rhombs, m.p. 204 °C identical with that obtained from the parent triazene. This ready fission of the N–S bond in presence of acid makes it possible that the

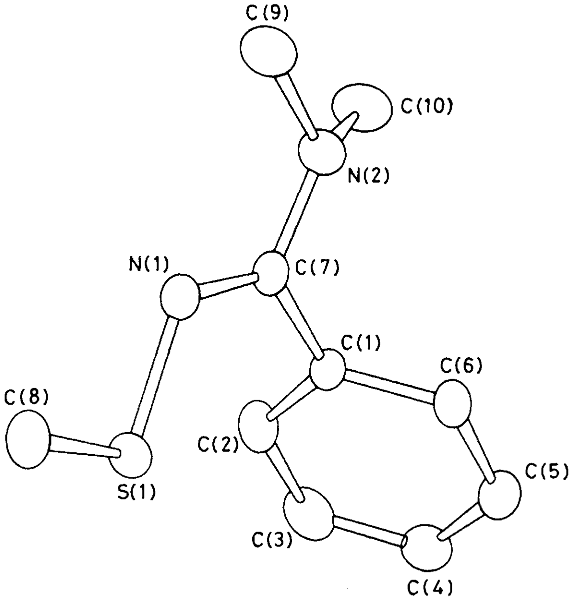


Figure 1. Crystal structure of *N*^{1},*N*^{1}-dimethyl-*N*^{2}-methylthiobenzamidine (**2a**).

sulphenamidine, like its precursor,[1] can be used as a sulphenylating agent.

All the above compounds give satisfactory elemental analyses. These sulphenamidines are, apparently, the first to be reported, and so we determined the crystal structure of compound (**2a**).† The *X*-ray diffraction data, collected at 178 K, yielded the structure shown in Figure 1. Although a detailed description will be published later, comparison with the structure of the parent triazene (**1a**)[2] shows that the backbone R^3–S–N=C–N remains a (nearly) planar zig-zag chain, but the amino-group is no longer planar.

Under analogous conditions, the aliphatic triazene (**1**; $R^1 = R^2 =$ Me, $R^3 =$ Et) likewise gave nitrogen evolution, but the solution darkened owing to the formation of a copper complex, which was then decomposed with aqueous ethylenediamine solution. The organic layer gave no sulphenamidine, but diethyl disulphide was isolated in fair yield. This may indicate that the mechanism involves free radicals which form a tight pair in the case of the aryl triazenes, but which dimerise with the aliphatic precursor. A copper derivative, acting in a redox system, may take part.

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† *Crystal data:* $C_{10}H_{14}N_2S$, $M = 194.3$, orthorhombic, $a = 5.894(4)$, $b = 8.227(4)$, $c = 21.067(6)$ Å, $U = 1021.5$ Å^3, $D_c = 1.26$, $Z = 4$, $F(000) = 416$, Mo-K_α radiation, $\lambda = 0.71069$ Å, μ(Mo-K_α) $= 3.0$ cm^{-1}, space group $P2_12_12_1$ (No. 19), 1457 reflexions with $F > 3\sigma(F)$, $R = 3.9\%$.

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.

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