

Novel Preparation of 1,3,5-Thiadiazine Derivatives by Cyclocondensation of Carbon Disulphide with Dialkylcyanamides under High Pressure

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At 500 MPa, 1 mol equiv. of carbon disulphide condenses with 3 mol equiv. of dialkylcyanamide to afford 2,6-bis(dialkylamino)-4-dialkylthiocarbamoylimino-1,3,5-thiadiazine, the structure of which was determined by X-ray crystallography.

Although at high pressure carbon disulphide gives various condensation products (e.g. a semiconducting and a low-conducting solid¹ and, in the presence of electron deficient acetylenes, tetrathiafulvalenes²) few reactions with nitriles have been reported. Recently we have shown that at high pressure, substituted cyanamides are as good dipolarophiles as electron deficient acetylenes.³ Here we report the condensation of carbon disulphide with dialkylcyanamides at high pressure to give novel 1,3,5-thiadiazines.

A typical experimental procedure was as follows: dimethylcyanamide was compressed in an excess of carbon disulphide (500 MPa,⁴ 100 °C, 20 h) to afford crystalline 2,6-bis(dimethylamino)-4-dimethylthiocarbamoylimino-1,3,5-thiadiazine † (**1a**) (84%⁵) as the main product. Two minor products were ob-

Table. Effects of temperature, pressure, and alkyl group on the yields of products.

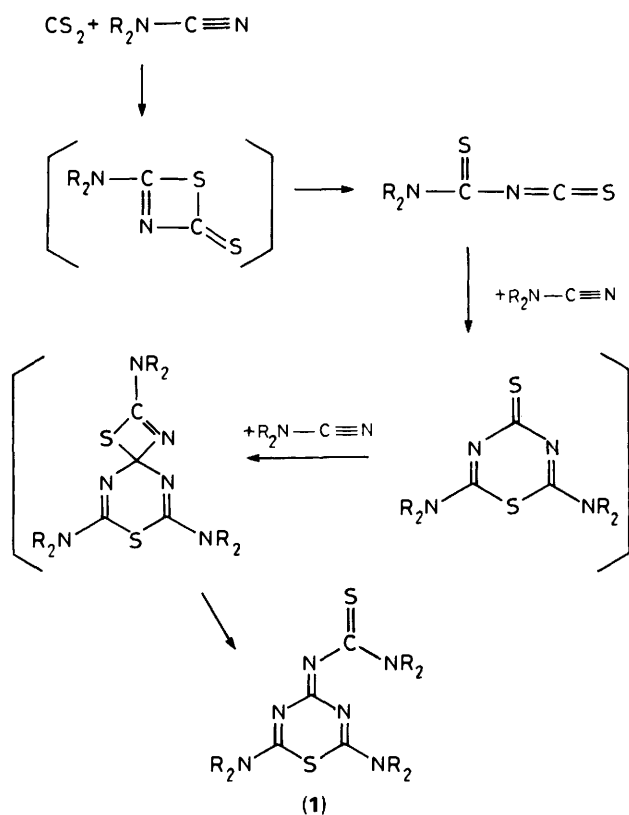
R ₂ N	Temp. (°C)	Pressure (MPa)	Yield of products (%)			
NMe ₂	50	800	(1a) 4.7	(2) 1.4	(3) 1.5	
	100	800	72	12	11	
	100	500	84	4.6	5.5	
	100	200	16	7	0.7	
1-Pyrrolidino	50	800	(1b) 71	Nd*	Nd	
1-Piperidino	70	800	(1c) 55	Nd	Nd	

Dialkylcyanamide 10 mmol, carbon disulphide 30 mmol, 20 h. * Nd = Not determined.

† Selected spectral data: (**1a**) m.p. 257.5 °C (ethanol); *m/z* 286 (*M*⁺), 242, 198, and 88 (100%); ν_{\max} (KBr) 1 640, 1 563, 1 546, 1 378, 1 285, 1 192, 1 108, 925, and 880 cm⁻¹; δ_{H} (Bruker AC 200, CDCl₃) 3.506 (s, 3 H, NCH₃), 3.200 (s, 12 H, NCH₃), and 3.132 (s, 3 H, NCH₃); δ_{C} 193.2 (C=S), 156.0 (2- and 6-ring carbon), 152.2 (4-ring carbon), 42.14, 39.58 (two methyl groups on thiocarbamoyl group), and 37.48 (br, 2- and 6-dimethylamino groups). Compounds (**1b**) and (**1c**) were also characterized by ¹H and ¹³C NMR, IR, and mass spectroscopy.

tained by preparative thin-layer chromatography of the mother liquor after treatment with water: 2,6-bis(dimethylamino)-[1,2,4]dithiazolo[1,5-*b*][1,2,4]dithiazole-6a-S^{IV} (**2**) (4.6%)⁵, m.p. 286 °C (lit.,⁶ 288 °C), and 5-dimethylamino-1,2,4-dithiazole-3-thione (**3**) (5.5%)⁵ m.p. 176.8 °C (lit.,⁷ 177.5 °C). The Table shows the effects of temperature, pressure, and alkyl groups on the yields of the products.

The crystal structure of compound (**1a**) was determined by



Scheme.

X-ray crystallography; * the Figure is the ORTEP diagram of (1a). Although the detailed mechanism of the reaction is not established yet, compounds (1) must be produced by repeated cycloaddition-retroaddition as shown in the Scheme. A similar formation of 1,3,5-thiadiazine ring from dialkylcyanamide and hexafluorothioacetone at ambient pressure is known.⁸

* Crystal data. $C_{10}H_{18}N_6S_2$, $M = 286.4$, monoclinic, space group $P2_1/c$, $a = 9.455(1)$, $b = 10.760(2)$, $c = 14.526(3)$ Å, $\beta = 108.76(1)$, $V = 1399.3(6)$ Å³, $Z = 4$, $D_c = 1.36$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 3.66$ cm⁻¹, $F(000) = 608$. Cell parameters and data collection were performed with graphite monochromated Mo-K α radiation on a Enraf-Nonius CAD4 diffractometer. 2794 Independent reflections were used for the analysis. The structure was solved by MULTAN 78 program.⁹ The structure was refined by full-matrix least-squares methods. All hydrogen atoms were found in D-fourier method; hydrogen atoms were fixed in LS calculation. The final agreement factors were $R = 0.045$ ($w = 1$). All computations were performed on a FACOM M-380 computer using UNICS III system.¹⁰ Atomic co-ordinates, bond lengths, bond angles, and thermal parameters are available on request from the Cambridge Crystallographic Centre. [See 'Instructions for Authors (1990),' *J. Chem. Soc., Perkin Trans. 1*, 1990, Issue 1.]

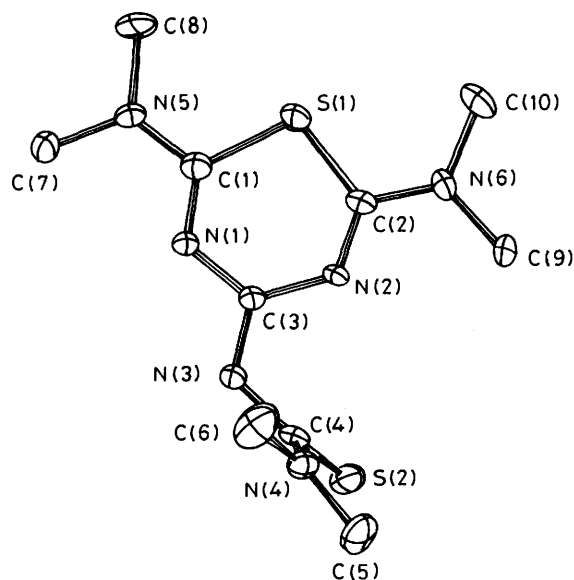


Figure. The molecular structure of (1a) giving the crystallographic numbering scheme. The 2- and 6-dimethylamino groups are almost flat and in the plane of the thiadiazine ring; the dihedral angle between the plane of dimethylthiocarbamoyl group and the thiadiazine ring was 72°.

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