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Novel Single Step Preparation of 1,3,5-Thiadiazin-4-ones from Carbon Oxide Sulfide and Dialkylcyanamides under High Pressure

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At 800 MPa, 130 °C carbon oxide sulfide condensed with dialkylcyanamide to afford 2,6-bis(dialkylamino)-1,3,5-thiadiazin-4-ones in good yields.

Heterocumulenes (X=C=Y) are one of the most convenient building blocks for heterocycles so that they have been widely employed (C=X and C=Y) as 2π addends in Diels-Alder reactions, dipolar cycloadditions or in [2+2] cycloadditions.1) From this view point it is surprising that the cycloaddition of carbon oxide sulfide has been studied only in a couple of exceptional systems.2) We believe that the limited reports are due to the gaseous character and the toxicity of carbon oxide sulfide.3)

Here we report a cyclocondensation of dialkylcyanamides with carbon oxide sulfide at high pressure in toluene solution. The reactions afforded 2,6-bis(dialkylamino)-1,3,5-thiadiazin-4-ones in excellent yields as the sole products.

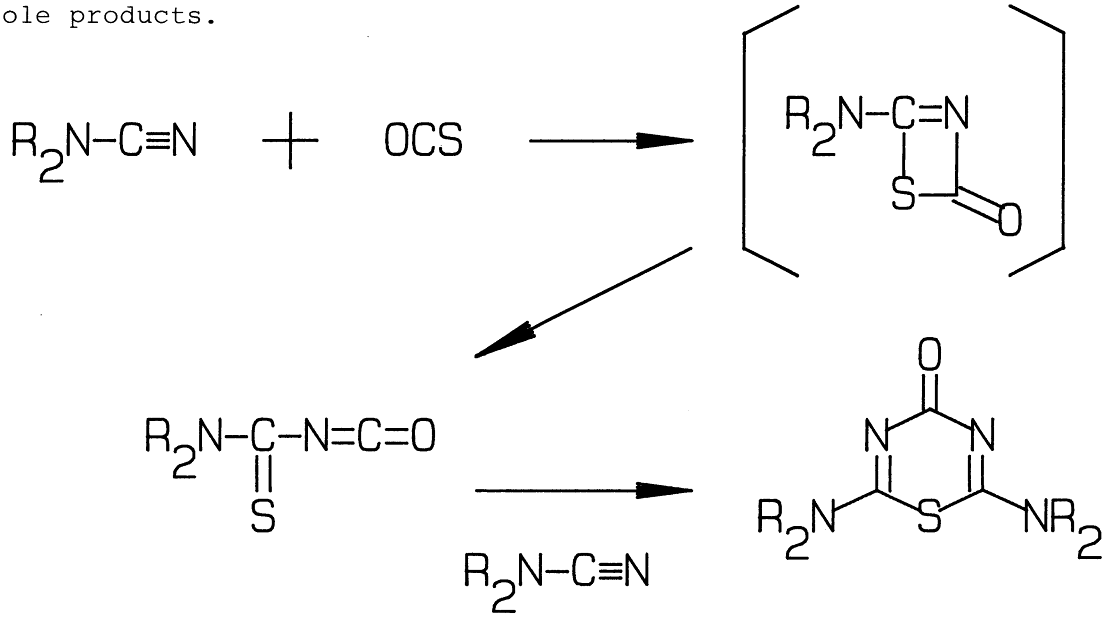
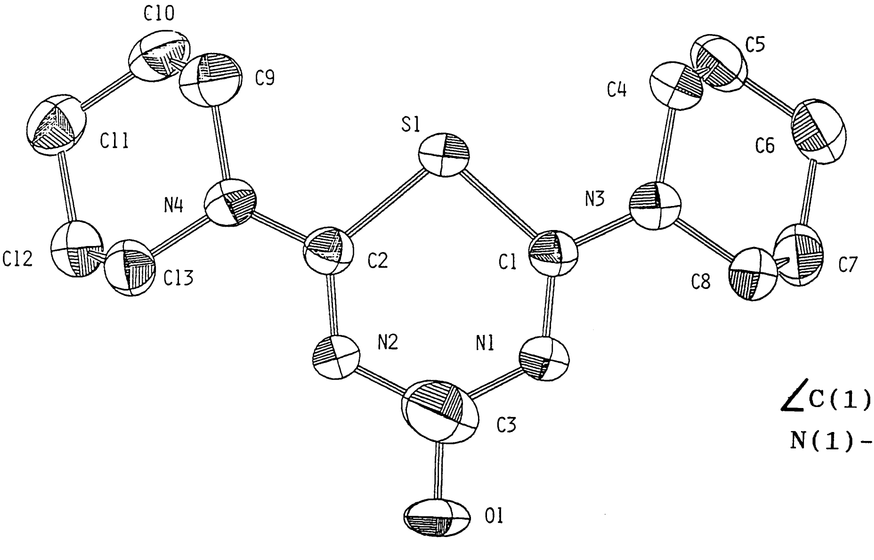


Table 1. Effects of Temperature, Pressure and Alkyl Group on the Yield of Compound 1[a)]

R_2N	Temperature °C	Pressure MPa	Yield of $1^{b)}$/%	
NMe_2	130	800	**1a**	92
	130	400		33
	130	200		7
	130	3		0
	100	1250		29
	100	800		14
	100	530		7
1-Pyrrolidinyl	130	800	**1b**	74
Piperidino	160	800	**1c**	94
	130	800		67
	100	800		13
Morpholino	130	800	**1d**	77

a) Molar ratio: R_2NCN/COS = 1.2, solvent: toluene, 20 h.
b) Isolated yield based on R_2NCN.



S(1)-C(1), 1.771(5);
C(1)-N(1), 1.270(6);
N(1)-C(3), 1.399(9);
C(3)-O(1), 1.265(8);
O(1)-N(2), 1.400(8);
N(2)-C(2), 1.284(6);
C(2)-S(1), 1.782(6);
C(1)-N(3), 1.360(8);
C(2)-N(4), 1.329(7);
∠C(1)-S(1)-C(2), 98.2(2);
N(1)-C(3)-N(2), 125.0(1).

Fig.1. The molecular structure of 1c with crystallographic numberings, selected bond lengths (Å), and angles (degree). the methylene carbons C(4), C(8), C(9), and C(13) are almost in the plane of the thiadiazinone ring.

Typical reaction procedure is as follows: Dimethylcyanamide (11 mmol) was dissolved in toluene (10 ml)$^{4)}$ saturated with carbon oxide sulfide (ca. 9 mmol). The solution was sealed in a poly(tetrafluoroethylene) capsule and compressed to 800 MPa, and kept at 130 °C for 20 h.$^{5)}$ After evaporation of the solvent and the cyanamide under a reduced pressure, crystalline 2,6-bis(dimethylamino)-1,3,5-thiadiazin-4-one (1a)$^{6)}$ was obtained (92%,$^{7)}$ mp 214 °C(benzene)). Table 1 shows the effects of temperature, pressure and alkyl groups on the yield of thiadiazinones. It shows that both temperature and pressure are crucial for this reaction.

The crystal structure of compound 1c was determined by X-ray crystallography;$^{8)}$ the Figure 1 shows the ORTEP diagram of 1c.

The products 1were presumably produced by the repeated cycloaddition/reversion procedure shown in the Scheme. A similar pathway was previously reported in the reaction of carbon disulfide with dialkylcyanamides at 800 MPa.$^{9)}$ We believe that thiocarbonyl heterocumulenes (S=C=X) react with dialkylcyanamides via the common thiocarbamoyl isocyanate intermediates (R_2N-CS-N=C=X)$^{10)}$ at high pressure.

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3) Carbon oxide sulfide (bp 49.9 °C) is supplied in a cylinder: see N. I. Sax and R. J. Lewis, "Dangerous Properties of Industrial Materials," Van Nostrand Reinhold, New York (1989), Vol, II, p.718.

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6) Compound 1a mp 214 °C(benzene); m/z 200 (M^+), 130 (100%); ν_{max}(KBr) 1580 cm^{-1}(C=O); δ_H(Burker AC 200, $CDCl_3$) 3.24 (6H, broad s, methyl groups), δ_C 165.7 (C=O), 159.4 (C=N), 57.8 (methyl groups); Anal Found: C, 41.88; H, 5.98; N, 27.47%. Calcd for $C_7H_{12}N_4OS$: C, 41.98; H, 6.04; N, 27.98%. Compounds 1b, 1c, and 1d were also characterized by ^{1}H and ^{13}C NMR, IR, and mass spectroscopy. All new compounds afforded consistent elemental analysis results.

7) Yield based on dimethylcyanamide fed.

8) Crystal data of(**1c**): $C_{13}H_{20}N_4OS$, M=280.39, triclinic, space group $P\bar{1}$, a=8.416(2), b=8.901(2), c=10.215(4) Å, α=66.66(2), β=82.20(2), γ=85.90(2), V=699.6(4) $Å^3$, Z=2, D_c=1.329 g cm^{-3}, μ(Cu-K_α) =18.34 cm^{-1}, F(000) =300. Cell parameters and data collection were performed with graphite monochromated Cu-K_α(λ=1.5418 Å) radiation on an Enrauf-Nonius CAD4 diffractometer. For a fear of decomposition a sample crystal (0.4x0.4x0.2 mm) was sealed in a glass capillary tube. The empirical corrections for absorption (ψscan) were done. 1436 Independent reflections ($|F_0|>3\sigma|F_0|$) were used for the analysis. The structure was solved by MULTAN 78 program.11) 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=0.066 (R_w=0.063) ($w=1/(0.00225|F_0|^2-0.0104|F_0|+0.3673)$. All computations were performed on a FACOM M-380 computer using UNICS III system.12) Atomic co-ordinates, bond lengths, bond angles, and thermal parameters are available on request from the Cambridge Crystallographic Center.

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