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A Novel Preparation of 2-Imino-1,3-thiazetidines from Carbon Disulfide, Dialkylcyanamide, and Benzylideneaniline under High Pressure

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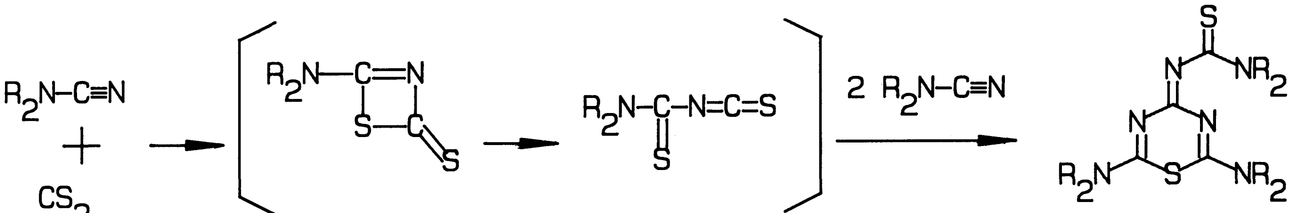
At 800 MPa, 100 °C carbon disulfide, dialkylcyanamide and benzylideneaniline afford 2-dialkylthiocarbamoylimino-3,4-diphenyl-1,3-thiazetidine, the structure of which was determined by X-ray crystallography.

Recently we have shown that carbon disulfide is a convenient building block for heterocyclic compounds, especially under high pressure.[1,2] For example at 500 MPa, 70 °C one molecule of carbon disulfide condensed with three molecules of dialkylcyanamide to afford 2,6-bis(dialkylamino)-4-dialkylthiocarbamoylimino-1,3,5-thiadiazine (1) in good yields.[1]



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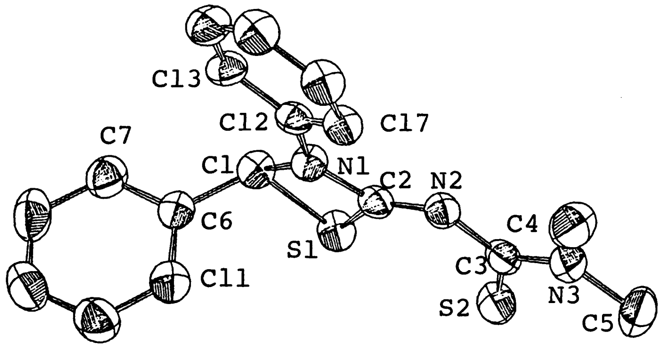
Here we report a convenient preparation of 2-dialkylthiocarbamoylimino-3,4-diphenyl-1,3-thiazetidines (2) from carbon disulfide, dialkylcyanamide, and benzylideneaniline under high pressure. The structure of an adduct 2 was determined by X-ray crystallography.

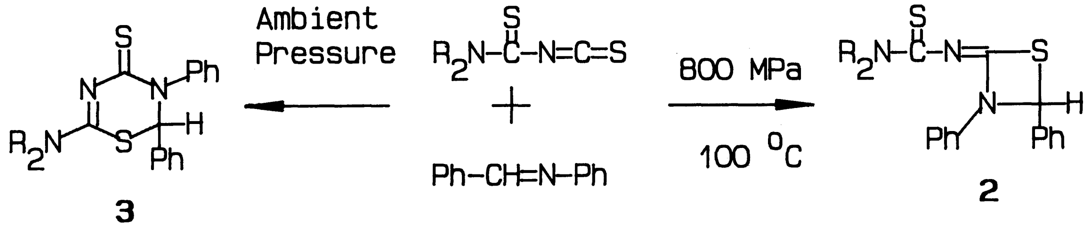
Typical procedure was as follows: at 800 MPa, 2 mmol of carbon disulfide, 1 mmol of dimethyl cyanamide and 0.5 mmol of benzylideneaniline were heated at 100 °C for 20 h.[3] The solid product thus formed was dissolved in dichloromethane (25 ml), and then was submitted to a short column of Al_2O_3 (100 g),[4] and eluted with dichloromethane (200 ml). The crystalline product (2a) recovered from the eluate was recrystallized from ethanol (84%).[5,6] The structure of this product (2a) was determined by X-ray crystallography to be 2-dimethylthiocarbamoylimino-3,4-diphenyl-1,3-thiazetidine (2a).[7] The Fig. 1 shows the ORTEP diagram of compound (2a).



S(1)-C(1), 1.880(4); N(1)-C(1), 1.474(4); N(1)-C(2), 1.356(4); S(1)-C(2), 1.762(3); N(2)-C(2), 1.280(4); ∠S(1)-C(2)-N(1), 96.6(2); C(2)-N(1)-C(1), 101.5(3); N(1)-C(1)-S(1), 87.8(2); C(1)-S(1)-C(1), 73.9(2).

Fig.1 The molecular structure of (2a) giving the crystallographic numbering scheme and selected bond length (Å) and angles (degree). The 2-dimethylthiocarbamoylimino and 3-phenyl groups are almost in the plane of thiazetidine ring.

This result clearly confirms that at high pressure carbon disulfide and dialkylcyanamides afford dialkyl-thiocarbamoyl isothiocyanates, which were assumed as key intermediates in the formation of 1,3,5-thiadiazine derivatives (1) in the previous paper.1)



The other results are summarized in the Table 1. High pressure is crucial for this reaction. Little effect of benzylideneaniline concentration on the yield of 2a indicates that at 100 °C the rate determining step for this cycloaddition is formation of dialkylthiocarbamoyl isothiocyanates. For the major product was compound 1a (R=CH_3) at 70 °C, formation of 2 must need higher temperature than that of 1.

Although Goerdeler reported that dialkylthiocarbamoyl isothiocyanates and benzylidene aniline afford [4+2] cycloadducts or 5,6-dihydro-5,6-diphenyl-2-dialkylamino-1,3,5-thiadiazine-4-thiones (3)8) at ambient pressure, compounds (3) are less stable than [2+2] cycloadducts (2) under the conditions used here.9) A similar [2+2] cycloaddition is observed in the reaction of p-toluenesulfonyl isothiocyanate with benzylidene aniline at ambient pressure.10) When 2-propylideneaniline, 1-phenylethylideneaniline or diphenylmethylideneaniline was used in place of benzylideneaniline in the present reaction, no significant product was obtained.

Table 1. Effects of temperature, pressure, alkyl group, and molar ratio on the yield of products.

R_2N-CN (equiv.)		CS_2 (equiv.)	PhNCHPh (equiv.)	Temp °C	Pressure MPa	Yield[a] of Products /%	
$(CH_3)_2N$	0.5	0.5	0.5	100	800	2a	30
	1.0	0.5	0.5	100	800		46
	0.5	1.0	0.5	100	800		58
	0.5	0.5	1.0	100	800		30[b]
	1.0	1.0	0.5	100	800		68
	1.0	2.0	0.5	100	800		84
	0.5	1.0	0.5	70	800		7
	0.5	1.0	0.5	100	600		53
	0.5	1.0	0.5	100	400		18
	0.5	1.0	0.5	100	200		3
$(C_2H_5)_2N$	1.0	2.0	0.5	100	800	2b	23
1-Pyrrolidinyl	1.0	2.0	0.5	100	800	2c	56
1-Piperidinyl	1.0	2.0	0.5	100	800	2d	52
1-Morpholinyl	1.0	2.0	0.5	100	800	2e	61

a) Yield based on benzylideneaniline fed.

b) Yield based on dimethylcyanamide fed.

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2) Y. Taguchi, M. Yasumoto, I. Shibuya, and Y. Suhara, Bull. Chem. Soc. Jpn., 62, 474 (1989); Y. Taguchi, K. Yanagiya, I. Shibuya, and Y. Suhara, ibid., 60, 727 (1987).

3) On the apparatus see, M. Kurabayashi, K. Yanagiya, and M. Yasumoto, Bull. Chem. Soc. Jpn., 44, 3413 (1971); polytetrafluoroethylene capsules were used in this work.

4) Aluminium oxide 90 (activity grade II-III) E. Merck art. 1097.

5) Yield based on benzylideneaniline fed.

6) Compound 2a: mp 171.8 °C (ethanol); mass spectrum m/z 327 (M^+), 181 (100%); ^{1}H-NMR($CDCl_3$)δ 7.47-7.21 (m, 9H, Ph), 7.03 (t, 1H, Ph), 6.23 (s, 1H, $C\underline{H}$-Ph), 3.46 (s, 3H, N-CH_3), 3.44 (s, 3H, N-CH_3); ^{13}C-NMR($CDCl_3$) δ 188.37 (C=S), 168.55 (C=N), 138.68, 135.66, 129.19, 129.09, 129.00, 126.47, 123.76, 118.22 (phenyl carbons), 72.51 ($\underline{C}$H-Ph), 41.32, 39.67

(N-CH_3); Anal. Found: C, 62.42; H, 5.24, N, 12.93%. Calcd for $C_{17}H_{17}N_3S_2$: C, 62.35; H, 5.23; N, 12.83%.

Compound 2b: mp 122.2 °C (ethanol); mass spectrum m/z 355 (M^+), 181 (100%); ^{13}C-NMR($CDCl_3$) δ 187.01 (C=S), 168.59 (C=N), 72.71 (CH-Ph); Anal Found: C, 63.89; H, 5.83; N, 11.83%. Calcd for $C_{19}H_{21}N_3S_2$: C, 64.19; H, 5.95; N, 11.82%.

Compound 2c: mp 202.9 °C (ethanol); mass spectrum m/z 353(M^+), 181(100%); ^{13}C-NMR($CDCl_3$) δ 184.81 (C=S), 167.30 (C=N), 72.35 (CH-Ph); Anal Found: C, 64.59; H, 5.57; N, 11.90%. Calcd for $C_{19}H_{19}N_3S_2$: C, 64.55; H, 5.42; N, 11.89%.

Compound 2d: mp 181.3 °C (ethanol); mass spectrum m/z 367(M^+), 186, 181(100%) ^{13}C-NMR($CDCl_3$) δ 186.66 (C=S), 169.66 (C=N), 72.58 (CH-Ph); Anal Found: C, 65.20; H, 5.80; N, 11.46%. calcd for $C_{20}H_{21}N_3S_2$: C, 65.36; H, 5.76; N, 11.43%.

Compound 2e: mp 181.5 °C (ethanol); mass spectrum m/z 369(M^+), 181(100%); ^{13}C-NMR($CDCl_3$) δ 188.16 (C=S), 170.10 (C=N), 72.45 (CH-PH); Anal Found: C, 61.69; H, 5.27; N, 11.36%. Calcd for $C_{19}H_{19}N_3OS_2$: C, 61.76, H, 5.18; N, 11.37%.

7) Crystal data: $C_{17}H_{17}N_3S_2$, M=327.47, monoclinic, space group $P2_1/n$, a=5.909(1), b=8.532(1), c=33.04(1)Å, β=92.70(1)°, V=1663.9(4) Å^3, Z=4, D_C=1.307 g cm^{-3}, (Cu-Kα)=1.54178Å, F(0,0,0)=688. Cell parameters and data collection were performed with graphite monochromated Cu-Kα radiation on a Enrauf-Nonius CAD4 diffractometer. 2857 independent reflections were collected and 2321 with $|F_o|>3\sigma(|F_o|)$ were used for the analysis. The structure was solved by MULTAN-78 program.[11)] The structure was refined by full-matrix least-squares method. All hydrogen atoms except one on the thiazetidine ring were found in D-Fourier method. The final agreement factors were R=0.055 (R_w=0.062). All computations were performed on a FACOM M-380 computer using UNICS-III system.[12)]

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9) When compound (3a, R=CH_3) dissolved in dimethylcyanamide was treated at 800 MPa, 100 °C for 20 h, it decomposed into miscellaneous products besides a small amount of compound (2a).

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