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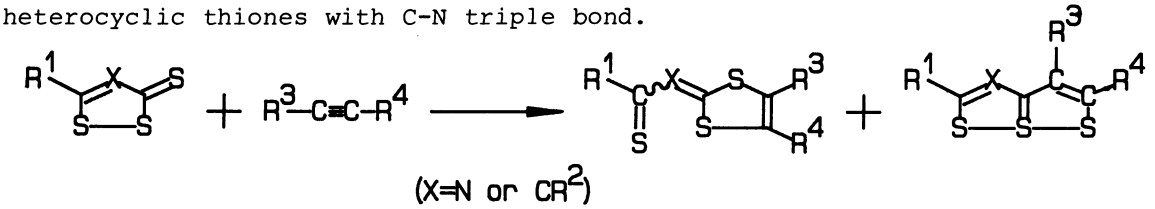
Cycloaddition of 5-Dialkylamino-1,2,4-dithiazole-3-thione with Dialkylcyanamide under High Pressure

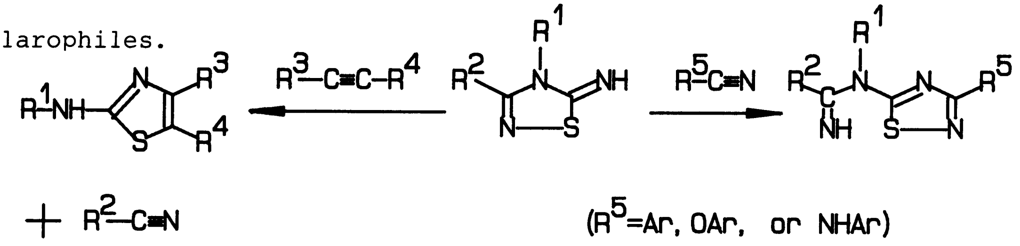
Tohru TSUCHIYA,* Masahiko YASUMOTO, and Isao SHIBUYA
National Chemical Laboratory for Industry,
Higashi 1-1, Tsukuba, Ibaraki 305

The title reaction at 800 MPa, 70 °C, give 5-imino-1,4,2-dithiazoles, formed through 1,3-dipolar cycloaddition. These adducts decompose to the reactants on heating at ambient pressure. At 160 °C and 800 MPa, the reaction give thermally stable [1,2,4]dithiazolo[1,5-b][1,2,4]dithiazole-6a-S^{IV} derivatives.

Cycloadditions of 1,2-dithiole-3-thiones or 1,2,4-dithiazole-3-thiones with activated acetylenes have been investigated by a number of researchers in the past three decades.[1)] These reactions gave mainly 1,3-dithiole derivatives through 1,3-dipolar cycloaddition at two sulfur atoms; in some cases [1,2]dithiolo[1,5-b][1,2]dithioles or their 3-aza analogues were also obtained, although there had been few reports dealing with the cycloaddition of these heterocyclic thiones with C-N triple bond.


(X=N or CR^2)

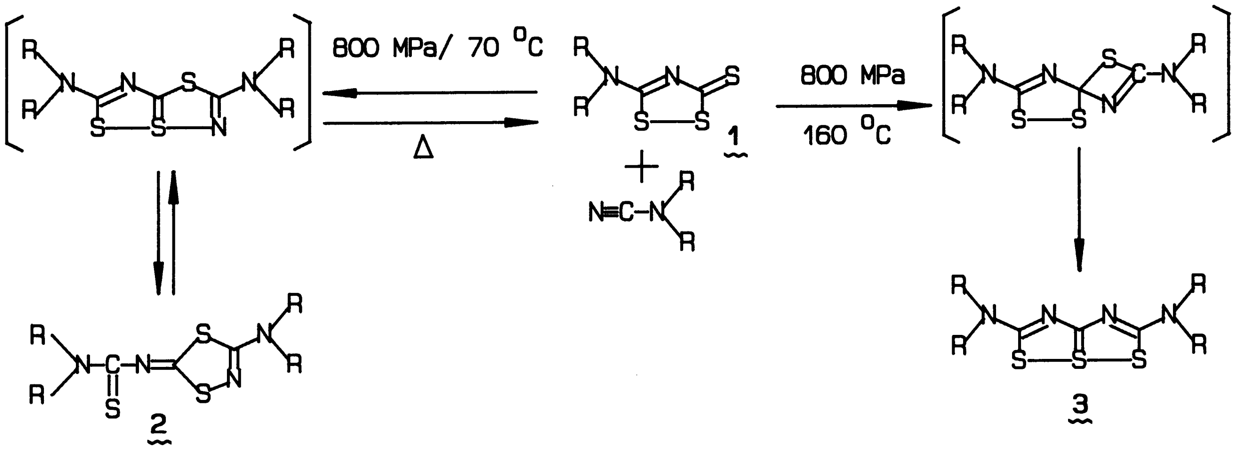
On the other hand, one of us reported that 5-imino-1,2,4-thiadiazolines formed cycloadducts with nitriles as well as with activated acetylenes.[2)] This finding indicates a similarity between C-N and C-C triple bonds as dipolarophiles.

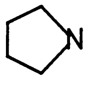
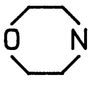

(R^5=Ar, OAr, or NHAr)

These facts prompted us to study the effects of pressure on these cycloadditions, because in concerted additions, it is expected that compression promotes the formation of adducts. Here we report the reaction of 5-dialkylamino-1,2,4-dithiazole-3-thiones with dialkylcyanamides at 800 MPa.

5-Dialkylamino-1,2,4-dithiazole-3-thiones(**1a**,**b**)[3] reacted with dialkylcyanamide at 70 °C/800 MPa,[4] affording cycloadducts 5-dialkylthiocarbamoylimino-3-dialkylamino-1,4,2-dithiazoles(**2a**,**b**).[5,6] At ambient pressure, these adducts decomposed to **1** and the corresponding cyanamides quantitatively on heating above their melting points or kept in chloroform-d_1 solutions for a week at room temperature. On the other hand at 160 °C/800 MPa, the same combination of **1a**-**c** and dialkylcyanamides gave 2,5-bis(dialkylamino)[1,2,4]dithiazolo[1,5-b][1,2,4]dithiazole-6a-S^{IV}(3a-c),[7-9] which are thermally stable isomers of **2**.

The production of **2** at lower temperature is clearly interpreted in terms of 1,3-dipolar cycloaddition of **1** with cyanamides. At elevated temperatures formation of **2** (thermally less stable) is unfavorable even at 800 MPa, consequently **3** (thermally more stable) become the sole products. The formation of **3** can be interpreted in terms of [2+2] cycloaddition of **1** with cyanamides.



R_2N	Yield of 2 /%		Yield of 3 /%	
Me_2N	**2a**	40	**3a**	37
	**2b**	77	**3b**	64
	No reaction		**3c**	4.5

In summary, we have shown that disubstituted cyanamides are dipolarophiles similar to acetylenes in the reactions with 1,2,4-dithiazole-3-thiones. It has been proved that application of high pressure is a powerful tool also in this cycloaddition.

References

1) A. Dibo, M. Stavaux, N. Lozac'h, and A. Hordvik, Acta Chem. Scand., Ser. B, 39, 103 (1985); C. Th. Pedersen, "Advances in Heterocyclic Chemistry, Vol. 31," ed by A. R. Katritzky, Academic Press, New York(1982), Chap. 2, pp. 95-103; J. Vialle, Q. Rep. Sulfur Chem., 5, 151 (1970).

2) Y. Yamamoto, T. Tsuchiya, M. Ochiumi, S-i. Arai, N. Inamoto, and K-y. Akiba, Bull. Chem. Soc. Jpn., 62, 211 (1989); K-y. Akiba, S. Arai, T. Tsuchiya, Y. Yamamoto, and F. Iwasaki, Angew. Chem., Int. Ed. Engl., 18, 166 (1979); K-y. Akiba, T. Tsuchiya, N. Inamoto, K. Yamada, H. Tanaka, and H. Kawazura, Tetrahedron Lett., 1976, 3819; K-y. Akiba, T. Tsuchiya, and N. Inamoto, ibid., 1976, 1877; K-y. Akiba, T. Tsuchiya, M. Ochiumi, and N. Inamoto, ibid., 1975, 455; K-y. Akiba, M. Ochiumi, T. Tsuchiya, and N. Inamoto, ibid., 1975, 459.

3) J. E. Oliver, R. T. Brown, and N. L. Redearu, J. Heterocycl. Chem., 9, 447(1972).

4) On the apparatus see M. Kurabayashi, K. Yanagiya, and M. Yasumoto, Bull. Chem. Soc. Jpn., 44, 3413 (1971). Polytetrafluoroethylene capsule was used.

5) After removal of cyanamides the residual solids were subjected to Al_2O_3 dry columns and eluted with benzene to give **2** along with recovered **1**.

6) Compound **2a**: yellow crystal, mp 127 °C (ethanol); mass spectrum m/e 248(M^+), 178(100%), 145, 114, 102, 99, 88; IR (KBr) 2935, 1572, 1464, 1377, 1272, 1170, 1128, 806, 513, 477 cm^{-1}; ^1H-NMR($CDCl_3$) δ 3.41 (s, 3H, N-CH_3), 3.38 (s, 3H, N-CH_3), 3.10 (s, 6H, N-CH_3); ^{13}C-NMR($CDCl_3$) δ 194.23 (broad, 5-), 185.73 (C=S), 155.43 (broad, 3-), 42.40, 39.75 (thiocarbamoyl N-CH_3), 39.80 (5- N-CH_3); Anal. Found: C, 33.90; H, 4.84; N, 22.43; S, 38.80%. Calcd for $C_7H_{12}N_4S_3$: C, 33.85; H, 4.87; N, 22.56; S, 38.73%.

Compound **2b**: yellow crystal, mp 138 °C; mass spectrum m/e 300(M^+), 204, 171, 114, 102, 96; IR (KBr) 2968, 2852, 1558, 1490, 1434, 1337, 1211, 786, 471 cm^{-1}; ^1H-NMR($CDCl_3$) δ 3.83-3.68 (m, 4H, N-CH_2-), 3.56-3.54 (m, 4H, N-CH_2-),

2.07-1.94 (m, 8H, -CH$_2$-); ^{13}C-NMR(CDCl$_3$) δ 193.44 (broad, 5-), 182.20 (C=S), 152.49 (broad, 3-), 51.82, 49.91 (thiocarbamoyl N-CH$_2$-), 49.17 (5- N-CH$_2$-), 25.74, 24.91 (thiocarbamoyl -CH$_2$-), 25.57 (5- -CH$_2$-); Anal. Found: C, 44.00, H, 5.38; N, 18.68; S, 31.71%. Calcd for $C_{11}H_{16}N_4S_3$: C, 43.97; H, 5.37; N, 18.65; S, 32.02%. Compound **1c** did not react with 1-morpholinocarbonitrile at 70 °C, mainly because of its low solubility.

7) Compound **3a**: mp 227-228 °C(ethanol); lit. 226 °C(DMF-water) by B. Stelander, H. G. Viehe, M. van Meerssche, G. Germain, and J. P. Declercq, Bull. Soc. Chim. Belg., 86, 291 (1977).

8) Compound **3b**: pale yellow crystal, mp 244.3 °C(ethanol); mass spectrum m/e 300(M^+), 231, 114, 72, 70(100%); IR (KBr) 2930, 2836, 1523, 1468, 1407, 1328, 1257, 1224, 647 cm^{-1}; ^{1}H-NMR(CDCl$_3$) δ 3.91-3.84 (m, 4H, N-CH$_2$-), 3.58-3.51 (m, 4H, N-CH$_2$-), 2.11-1.94 (m, 8H, -CH$_2$-); ^{13}C-NMR(CDCl$_3$) δ 185.84 (2,5-), 179.46 (3a-), 50.65, 50.17 (N-CH$_2$-), 25.55, 25.27 (-CH$_2$-); Anal. Found: C, 43.73; H, 5.43; N, 18.52; S, 31.66%. Calcd for $C_{11}H_{16}N_4S_3$: C, 43.97; H, 5.37; N, 18.65; S, 32.02%.

Compound **3c**: pale yellow needle, mp 242.3 °C(ethanol); mass spectrum m/e 332(M^+), 247, 130, 86(100%); IR (KBr) 2848, 1508, 1418, 1276, 1245, 1105, 1025, 925, 901 cm^{-1}; ^{1}H-NMR(CDCl$_3$) δ 4.11 (broad s, 4H, N-CH$_2$-), 3.78 (broad s, 12H, N-CH$_2$- and O-CH$_2$-); ^{13}C-NMR(CDCl$_3$) δ 187.96 (3a-), 183.00 (2,5-), 66.39 (broad, O-CH$_2$-), 49.64, 47.64 (broad, N-CH$_2$-); Anal. Found: C, 39.58; H, 4.82; N, 16.81; S, 28.68%. Calcd for $C_{11}H_{16}N_4O_2S_3$: C, 39.74; H, 4.85; N, 16.85; S, 28.93%. 62% of **1c** used was recovered.

9) The reaction mixtures were subjected to SiO_2 dry columns and were eluted with diethyl ether to afford **3** along with 2,4,6-tris(dialkylamino)-1,3,5-triazines.

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