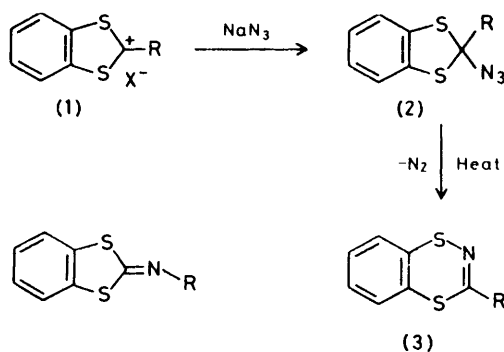


General Synthesis of 1,4,2-Benzodithiazines by Thermolysis of 1,3-Benzodithiol-2-yl Azides

By Juzo Nakayama,* Michihiro Ochiai, Kaoru Kawada, and Masamatsu Hoshino, Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338, Japan

Thermal decomposition of a variety of 1,3-benzodithiol-2-yl azides (2), easily obtainable from 1,3-benzodithiolylium salts and sodium azide, gives 1,4,2-benzodithiazines (3) in good yields, thus providing a general synthetic route to these compounds.

ALTHOUGH the synthesis and physical and chemical properties of 1,4-dithiins have been extensively investigated, studies on their aza-analogues, 1,4,2-dithiazines, are surprisingly scarce.¹ Fanghänel found that thermally



- (4) R = H
 (5) R = Ph
 (6) R = SMe

unstable 2-methylthio-1,3-dithiol-2-yl azides decompose to give mixtures of 3-methylthio-1,4,2-dithiazines and *N*-methylthio-2-imino-1,3-dithioles, while the thermolysis of the more stable 4,5-tetramethylene-1,3-dithiol-2-yl azide proceeds in a less distinct way to afford 5,6-tetramethylene-1,4,2-dithiazine only in 10.5% yield.^{1c} We report the general synthesis of 1,4,2-benzodithiazines (3) by thermal decomposition of 1,3-benzodithiol-2-yl azides (2). In the present study, 1,4,2-benzodithiazines (3) are usually the sole product and could be easily isolated in good yields.

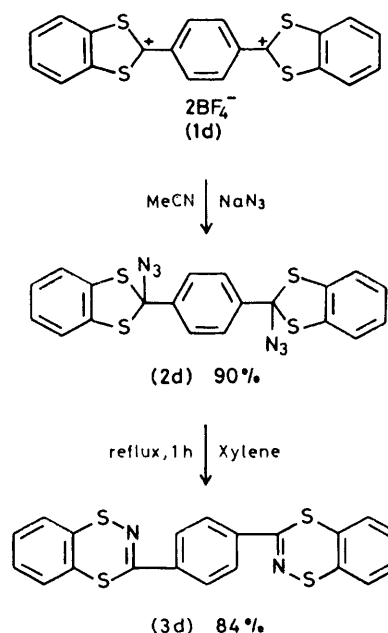
RESULTS AND DISCUSSION

1,3-Benzodithiol-2-yl azide (2a) is readily obtained by treatment of 1,3-benzodithiolylium tetrafluoroborate (1a) with sodium azide.² Heating (2a) in boiling toluene for 2 h gave 1,4,2-benzodithiazine (3a) in a 90% yield. The structure of (3a) was determined by elemental analysis and spectroscopic data. The isomeric structure (4) was ruled out since the compound does not show the absorption due to the N-H bond in its i.r. spectrum. Similarly, the thermolyses of 2-aryl-1,3-benzodithiol-2-yl azides (2b, c), easily obtainable from the corresponding dithiolylium salts (1b, c), yielded the benzodithiazines (3b, c) nearly quantitatively. The starting compounds

(1b, c) were prepared in good yields by treatment of the corresponding 2-aryl-1,3-benzodithioles with trityl salt. In the thermolysis of (2b), the formation of the isomeric compound (5) of (3b) was not detected at all. Compound (5) was synthesized by condensation of 2-methylthio-1,3-benzodithiolylium perchlorate (1h) with aniline. The reaction could also be satisfactorily applied to the bis-azide (2d), which was easily obtained from the bis-tetrafluoroborate (1d).

The dithiolylium salts (1e-g), which were highly stabilised by a strongly electron-donating substituent at the 2-position, did not react with sodium azide to give the covalent azides. However, they could be converted into the corresponding dithiazines (3e-g) by heating them with sodium azide in boiling acetonitrile. Evidently, in these cases, the decomposition reaction proceeds *via* the covalent azide existing in a small amount in an equilibrium mixture.

The azide (2h) from 2-methylthio-1,3-benzodithiolylium perchlorate (1h) is thermally unstable, and heating



(1h) and sodium azide at 50 °C in acetonitrile gave the dithiazine (3h) (37%) and the dithiole (6) (48%), in agreement with the results of Fanghänel.^{1c}

An attempt to prepare 1,4,2-dithiazine by thermolysis of 1,3-dithiol-2-yl azide ² was unsuccessful. The reaction gave an intractable oil.

The results described above clearly show that insertion of the nitrogen into the C-S bond predominates over insertion into the C-H, C-C, and C-N bonds. Thus, the present method provides a versatile general synthesis of (3) since the starting dithiolylium salts (1) have recently

Synthesis of 1,4,2-benzodithiazines (3)

Starting material	Yield of (2) (%)	Yield of (3) (%)
(1a; R = H)	89	90
(1b; R = Ph)	90	93
(1c; R = C ₆ H ₄ OMe- <i>p</i>)	92	99
(1c; R = C ₆ H ₄ NMe ₂ - <i>p</i>)	*	51
(1f; R = indol-3-yl)	*	50
(1g; R = morpholino)	*	19
(1h; R = SMe)	*	37

* Not isolated.

become readily obtainable, and the thermal decomposition only gives the ring-expansion products (3), except when the substituent at the 2-position is methylthio.

The present ring-expansion reaction could not be achieved photolytically. The photolysis of (2a) in hexane gave only polymeric compounds.

EXPERIMENTAL

I.r. spectra of solids were taken for KBr discs, and those of liquids for films, using a JASCO IRA-2 spectrometer. ¹H N.m.r. spectra were determined for CDCl₃ solutions, unless otherwise stated, by a Varian A-60D spectrometer or a Hitachi R24B spectrometer with tetramethylsilane as internal reference. All melting points are uncorrected and were determined on a Mel-Temp melting-point apparatus. For silica gel chromatography, Merck Art 7734 (E. Merck, Darmstadt) was used. Acetonitrile was refluxed over and distilled from calcium hydride, and stored over molecular sieves.

1,4,2-Benzodithiazine (3a).—A solution of 1,3-benzodithiol-2-yl azide ² (2a) (1.95 g, 10 mmol) in toluene (100 ml) was refluxed for 2 h. The resulting pale yellow solution was evaporated under reduced pressure and the residual oil was purified by silica gel chromatography with benzene as eluant to give (3a) (1.51 g, 90%) as a pale yellow oil, b.p. 100–101 °C at 1 mmHg (Found: C, 50.3; H, 2.95; N, 8.4; S, 37.9. C₇H₅NS₂ requires C, 50.3; H, 3.0; N, 8.4; S, 38.3%); ν_{\max} 1 580, 1 540, 1 450, 1 430, 1 255, 845, 780, and 750 cm⁻¹; δ 6.9–7.3 (4 H, m) and 8.15 (1 H, s).

3-Phenyl-1,4,2-benzodithiazine (3b).—A solution of trityl tetrafluoroborate (3.63 g, 11 mmol) in acetonitrile (30 ml) was added to a stirred solution of 2-phenyl-1,3-benzodithiole ^{2,3} (2.30 g, 10 mmol) in acetonitrile (40 ml). The mixture was stirred for 2.5 h and diluted with anhydrous ether (100 ml). The resulting precipitate was collected and washed with ether to give 2-phenyl-1,3-benzodithiolylium tetrafluoroborate (1b) (2.77 g, 88%) as pale yellow crystals, m.p. 188 °C.

A mixture of (1b) (1.58 g, 5 mmol) and sodium azide (0.65 g, 10 mmol) was stirred for 2 h at room temperature and then diluted with cold water (20 ml). The resulting white precipitate was collected, washed with water, and dried to give 2-phenyl-1,3-benzodithiol-2-yl azide (2b) (1.28

g, 90%), m.p. 83 °C (decomp.), which was subjected to the thermolysis without further purification; ν_{\max} 2 100 cm⁻¹ (N₃); δ 6.9–7.5 (7 H, m) and 7.7–8.0 (2 H, m).

A solution of (2b) (813 mg, 3 mmol) in toluene (20 ml) was refluxed for 1 h and the toluene was removed under reduced pressure. The yellow residue was triturated with hexane (5 ml) and collected to give (3b) (675 mg, 93%), m.p. 43 °C, as yellow needles (from methanol) (Found: C, 64.1; H, 3.8; N, 5.7; S, 26.2. C₁₃H₉NS₂ requires C, 64.2; H, 3.75; N, 5.75; S, 26.3%); ν_{\max} 1 575, 1 540, 1 465, 1 230, 920, 765, and 695 cm⁻¹; δ 7.2–7.7 (7 H, m) and 7.9–8.2 (2 H, m).

3-(*p*-Methoxyphenyl)-1,4,2-benzodithiazine (3c).—2-(*p*-Methoxyphenyl)-1,3-benzodithiolylium tetrafluoroborate (1c) was prepared in 83% yield from 2-(*p*-methoxyphenyl)-1,3-benzodithiole ⁴ and trityl tetrafluoroborate.

2-(*p*-Methoxyphenyl)-1,3-benzodithiol-2-yl azide (2c) was prepared in 92% yield from (1c) and sodium azide, m.p. 74–75 °C (decomp.); ν_{\max} 2 050 cm⁻¹ (N₃); δ 3.80 (3 H, s), 6.8–7.1 and 7.75–8.05 (4 H, A₂B₂ m), and 7.1–7.4 (4 H, m).

The dithiazine (3c) was obtained in 99% yield by refluxing a benzene solution of (2c) for 3 h, m.p. 93 °C, yellow needles (from cyclohexane) (Found: C, 61.5; H, 4.05; N, 5.1. C₁₄H₁₁NOS₂ requires C, 61.55; H, 4.05; N, 5.15%); δ 3.80 (3 H, s), 6.8–7.0 and 7.9–8.1 (4 H, A₂B₂ m), and 7.38 (4 H, s).

1,4-Phenylene-3,3'-bis-(1,4,2-benzodithiazine) (3d).—A mixture of 167 mg (0.3 mmol) of 1,4-phenylene-2,2'-bis-(1,3-benzodithiolylium) bistetrafluoroborate ⁵ (1d) (167 mg, 0.3 mmol) and sodium azide (78 mg, 1.2 mmol) in acetonitrile (10 ml) was stirred for 1 h. The mixture was diluted with water and extracted with methylene chloride. The extract was washed with water, dried, and evaporated to give 1,4-phenylene-2,2'-bis-(2-azido-1,3-benzodithiole) (2d) (128 mg, 92%), which decomposed at 115–117 °C with evolution of gas and melted at 214–216 °C; ν_{\max} 2 100 cm⁻¹ (N₃).

A solution of (2d) (124 mg) in xylene (10 ml) was refluxed for 1 h to give (3d) (90 mg, 84%), m.p. 223–224 °C, yellow needles (from benzene) (Found: C, 58.9; H, 2.95; N, 6.85. C₂₀H₁₂N₂S₄ requires C, 58.8; H, 2.95; N, 6.85%); ν_{\max} 1 440, 1 215, 905, 835, and 735 cm⁻¹; δ 7.26 (8 H, s) and 8.02 (4 H, s).

3-(*p*-Dimethylaminophenyl)-1,4,2-benzodithiazine (3e).—A mixture of 2-(*p*-dimethylamino)phenyl-1,3-benzodithiolylium perchlorate ⁶ (1e) (1.12 g, 3 mmol) and sodium azide (0.22 g, 3 mmol) in acetonitrile (50 ml) was refluxed overnight. The mixture was diluted with cold water and extracted with methylene chloride. The extract was washed with water, dried, and evaporated. Silica gel chromatography of the residue, eluting with benzene, gave (3e) (0.44 g, 51%), m.p. 123 °C, yellow needles (from cyclohexane) (Found: C, 62.95; H, 4.9; N, 9.75. C₁₆H₁₄N₂S₂ requires C, 62.95; H, 4.9; N, 9.8%); δ 2.95 (6 H, s), 6.60 (2 H, d), 7.25 (4 H, s), and 7.25 (2 H, d).

3-Indol-3-yl-1,4,2-benzodithiazine (3f).—A mixture of 2-(3-indolyl)-1,3-benzodithiolylium tetrafluoroborate ⁷ (1.77 g, 5 mmol) (1f) and sodium azide (0.65 g, 10 mmol) in acetonitrile (150 ml) was refluxed for 10 h. The mixture was purified by silica gel chromatography (benzene as eluant) to give (3f) (0.73 g, 50%), m.p. 169–171 °C, yellow needles (from ethanol) (Found: C, 63.65; H, 3.45; N, 9.9. C₁₅H₁₀N₂S₂ requires C, 63.85; H, 3.55; N, 9.95%); ν_{\max} 3 200 cm⁻¹ (NH); δ ([²H₆]DMSO) 7.0–7.6 (7 H, m), 8.0–8.3 (2 H, m), and 12.8 (1 H, br s, NH).

3-Morpholino-1,4,2-benzodithiazine (3g).—A mixture of

morpholino-1,3-benzodithiolylium perchlorate⁸ (1g) (1.69 g, 5 mmol) and sodium azide (0.65 g, 10 mmol) in acetonitrile (50 ml) was refluxed for 1 h. The mixture was diluted with water and extracted with methylene chloride. The extract was washed with water, dried, evaporated, and recrystallized from hexane to give (3g) (0.24 g, 19%), m.p. 110.5–111.5 °C, pale yellow crystals (Found: C, 52.4; H, 4.75; N, 11.1. C₁₁H₁₂N₂OS₂ requires C, 52.4; H, 4.8; N, 11.1%); δ 3.65 (8 H, br s), and 7.2–7.5 (4 H, m).

3-Methylthio-1,4,2-benzodithiazine (3h) and N-Methylthio-2-imino-1,3-benzodithiole (6).—A mixture of 3-methylthio-1,3-benzodithiolylium perchlorate⁹ (1h) (1.49 g, 5 mmol) and sodium azide (0.65 g, 10 mmol) in acetonitrile (40 ml) was heated at 50 °C for 4 h. The mixture was poured into cold water and extracted with ether. The extract was washed with water, dried, and evaporated to give 0.98 g of oily product. Analysis by ¹H n.m.r. showed the oil to be a mixture of (3h) and (6) in a ratio of ca. 1 : 1.2. Purification of the oil by column chromatography (carbon tetrachloride as eluant) gave (3h) (0.39 g, 37%), m.p. 32 °C (lit.,^{1c} m.p. 32 °C); δ 2.50 (3 H, s) and 7.1–7.4 (4 H, m); and (6) (0.52 g, 48%), m.p. 62.5–64 °C (lit.,^{1c} m.p. 66 °C); δ 2.80 (3 H, s) and 7.0–7.4 (4 H, m).

N-Phenyl-2-imino-1,3-benzodithiole (5).—This compound has been prepared previously by thermolysis of 1,2,3-benzothiadiazole in the presence of phenyl isothiocyanate.¹⁰ A mixture of (1h) (1.49 g, 5 mmol), aniline (0.46 g, 5 mmol), and pyridine (0.5 ml) in acetonitrile (30 ml) was refluxed for 1 h. The mixture was diluted with water and the resulting crystalline precipitate was collected, washed with water, and dried to give crude product (1.13 g, 92%), which was recrystallized

from methanol to give pure (5), m.p. 68–69 °C (white flakes).

Thermolysis of 1,3-Dithiol-2-yl Azide.—A solution of the azide (0.37 g, 2.5 mmol) in benzene (50 ml) was refluxed for 5 h. Removal of benzene afforded resinous materials. Attempted purification was unsuccessful.

Photolysis of (2a).—A solution of (2a) (0.39 g, 2 mmol) in hexane (300 ml) was irradiated for 4 h with a 120-W high-pressure mercury-discharge lamp in a Pyrex apparatus. The resulting voluminous precipitate was collected to give polymeric material (0.07 g) and the filtrate was evaporated to give mainly the starting material. The use of acetone as solvent also failed to give the desired product (3a).

[0/688 Received, 12th May, 1980]

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