to slightly gray powdery solid had formed. The mixture was stirred for a further 30 min and filtered. The solid was dried in vacuo in a desiccator ($CaCl_2$), yield 95–99%. Infrared spectra indicated the absence of the N–H group.

***N*-Alkyl-*N*-*p*-toluenesulfonyl-2,4,6-trinitrobenzenesulfenamides.** A solution of 3.5 mmol of 2,4,6-trinitrobenzenesulfenyl chloride in 10 ml of benzene was added to a magnetically stirred suspension of 4 mmol of a silver salt of *N*-alkyl-*p*-toluenesulfonamide in 30 ml of benzene and the mixture was stirred at room temperature for 48 h. After filtration of the solid, the solution was evaporated and the residue chromatographed on silica gel with benzene–hexane (2:1) as an eluent. The products were purified by recrystallization from tetrahydrofuran–hexane (Table II).

Registry No. —**1**, 60882-88-4; **3**, 16158-74-0; **4**, 60882-89-5; **5**, 60882-90-8; NHR_1R_2 (R_1 = $CHMe_2$; R_2 = CH_2Ph), 102-97-6; NHR_1R_2 (R_1 = $CHMe_2$; R_2 = $CHMe_2$), 108-18-9; NHR_1R_2 (R_1 = CH_2Ph; R_2 = 2,4,6-$Me_3C_6H_2$), 60882-91-9; *p*-$MeC_6H_4SO_2NHR$ (R = CH_2Ph)·Ag, 60882-92-0; *p*-$MeC_6H_4SO_2NHR$ (R = CH_2Me_2)·Ag, 60882-93-1; *p*-$MeC_6H_4SO_2NHR$ (R = CHMePh)·Ag, 60882-94-2; *p*-$MeC_6H_4SO_2NHR$ (R = CMe_2CH_2OMe)·Ag, 60882-95-3; benzenesulfenyl chloride, 931-59-0; benzyl 2,4,6-trinitrobenzenesulfenate, 60882-96-4; benzyl alcohol, 100-51-6.

References and Notes

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Derivatives of 4-Chloro-3,5-dinitrobenzotrifluoride. 2. Synthesis of 2-(Trifluoromethyl)-4-nitrobenzimidazo[2,1-*b*]benzothiazole and Related Compounds[1]

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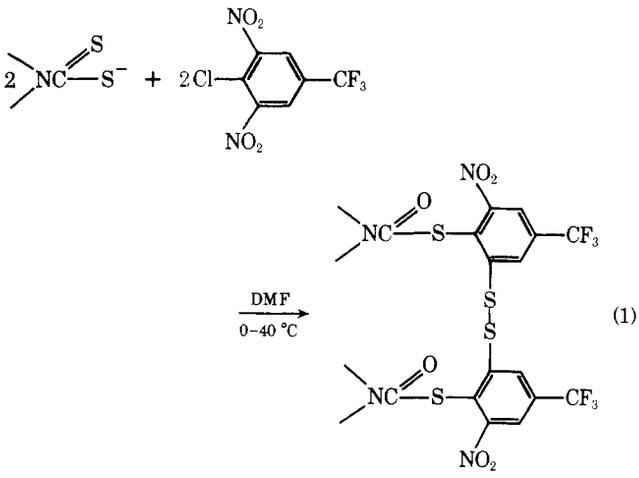
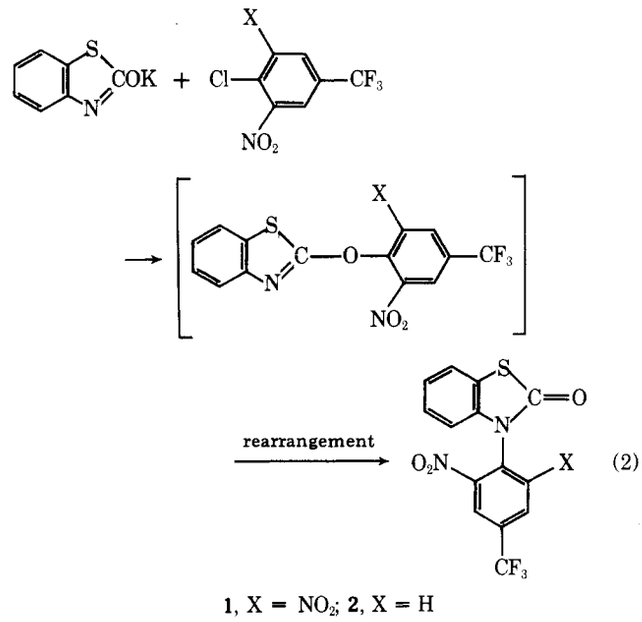
Depending on reaction temperatures the reaction of potassium 2-mercaptobenzimidazole with 4-chloro-3,5-dinitrobenzotrifluoride afforded either the expected 2-(2,6-dinitro-4-trifluoromethylphenylthio)benzimidazole (**3**) or the unexpected 4-nitrobenzimidazo[2,1-*b*]benzothiazole (**5**). Possible mechanism and supporting NMR, IR, and mass spectral data are discussed.

In a previous communication[2] we reported that the reaction of sodium or triethylamine salts of disubstituted dithiocarbamic acids with 4-chloro-3,5-dinitrobenzotrifluoride afforded the product as illustrated by reaction 1. Thus it appeared desirable to replace the above anion with other nucleophiles.



The reaction of potassium 2-benzothiazolol with 4-chloro-3,5-dinitrobenzotrifluoride or 4-chloro-3-nitrobenzotrifluoride in dimethylformamide at 90–100 °C afforded 3-(2,6-dinitro-4-trifluoromethylphenyl)-2-benzothiazolinone (**1**) and 3-(2-nitro-4-trifluoromethylphenyl)-2-benzothiazolinone (**2**),

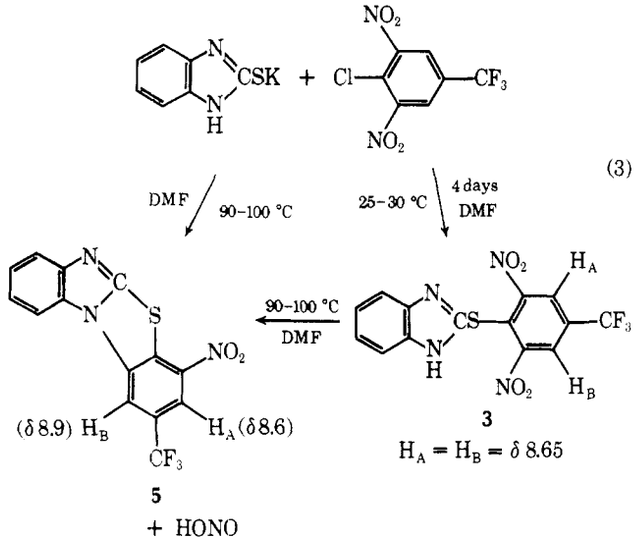


1, X = NO_2; **2**, X = H

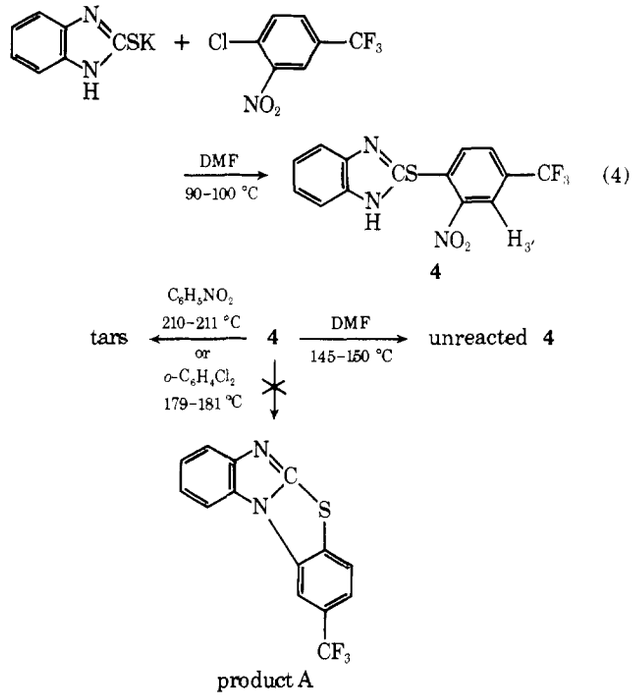
respectively (reaction 2). The NMR, IR, and mass spectral data for **1** and **2** were in agreement for the proposed structures.

Depending on reaction temperatures, the reaction of potassium 2-mercaptobenzimidazole with 4-chloro-3,5-dinitrobenzotrifluoride in dimethylformamide afforded either the

expected product, 2-(2,6-dinitro-4-trifluoromethylphenylthio)benzimidazole (3), at 25–30 °C or the cyclized product, 2-(trifluoromethyl)-4-nitrobenzimidazo[2,1-*b*]benzothiazole (5), at 90–100 °C. Heating 3 in dimethylformamide at 90–100 °C also furnished 5 (reaction 3). The reaction of potassium



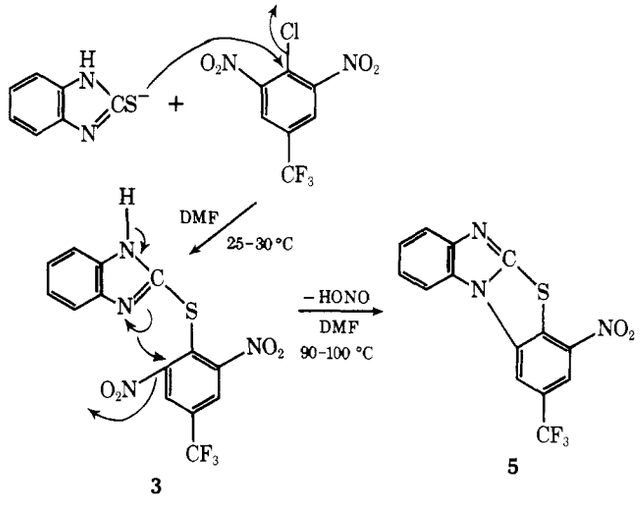
2-mercaptobenzimidazole with 4-chloro-3-nitrobenzotrifluoride in dimethylformamide at 90–100 °C did not afford the expected cyclized product A but instead furnished 2-(2-nitro-4-trifluoromethylphenylthio)benzimidazole (4). The heating of 4 in various solvents at reflux temperatures either gave unreacted 4 or decomposed products (reaction 4). Proof of structure for 3, 4, and 5 was based on elemental analysis,



NMR, IR, and mass spectral data. It is noteworthy to contrast the chemical shift for the aromatic protons (H_A and H_B) in 3 and 5. The H_A and H_B protons in 3 are equivalent and appeared at δ 8.65 whereas in 5 H_A H_B protons are nonequivalent and appeared at δ 8.6 and 8.9, respectively. The assignment of H_A and H_B protons in 5 seems logical since one would not expect the chemical shift of H_A to change significantly when 3 is converted to 5. However, the environment of the H_B proton changed markedly from 3 to 5. In 5, the H_B proton resides in the plane of the heteroaromatic moiety and would be expected to be deshielded with respect to its position in 3. This downfield shift of 0.25 ppm for H_B in 5 lends support for the cyclization reaction. Interpretation of the mass fragmentation patterns for 3, and 5 are depicted in Schemes I and II, respectively. See microfilm edition for these schemes.[3]

Fused rings containing the benzothiazolyl and benzimidazolyl moieties as in 5 have been prepared by other routes.[4]

We would like to propose the following scheme for the cyclization reaction:



Experimental Section

NMR spectra were obtained with a Varian A-60 NMR spectrometer. The chemical shifts are reported in δ, using tetramethylsilane as reference. All melting points were taken upon a Fisher-Johns block and are uncorrected. The mass spectra of 1–5 were determined with a Varian-MAT CH-7 mass spectrometer operating at an ionizing potential of 70 eV using the direct insertion probe technique with a source temperature of 250 °C. The infrared spectra of 2, 2, and 5 were obtained with a Beckman IR-12 spectrophotometer.

3-(2,6-Dinitro-4-trifluoromethylphenyl)-2-benzothiazolinone (1) and 3-(2-Nitro-4-trifluoromethylphenyl)-2-benzothiazolinone (2). To a stirred solution containing 15.1 g (0.1 mol) of 2-benzothiazolol and 6.6 g (0.1 mol) of 85% potassium hydroxide in 200 ml of DMF and 10 ml of water, 0.1 mol of 4-chloro-3,5-dinitrobenzotrifluoride or 4-chloro-3-nitrobenzotrifluoride was added in one portion. An exothermic reaction set in causing a temperature rise from 25 to 35 °C. The stirred reaction mixture was heated at 90–100 °C for 24 h. After cooling to 30 °C, 800 g of ice water was added and stirring continued at 0–10 °C for 1 h. The solids were collected by filtration, washed with water until the washings were neutral to litmus, and air dried at 25–30 °C. The crude product (1), mp 220–224 °C, was obtained in 73% yield. After recrystallization from toluene, 1 melted at 233–234 °C; NMR ($CDCl_3$) δ 7.05–7.70 (m, 4, H-4 to H-7), 8.66 (s, 2); IR (CSI) 3090 (ArC–H), 1695 and 1675 (C=O), 1560–1550 (NO_2 asymmetric), 1400–1100 (C–F), 1320–1310 (NO_2 symmetric), and 700–600 cm^{-1} (C–S); mass spectrum *m/e* (rel intensity) 385 (100), 366 (2), 339 (5), 311 (25), 293 (15), 265 (47), 253 (32), 196 (31), 96 (22), and 69 (19).

Anal. Calcd for $C_{14}H_6F_3N_3O_5S$: C, 43.64; H, 1.57; N, 10.91; S, 8.32. Found: C, 43.58; H, 1.57; N, 10.93; S, 8.41.

The crude product (2), mp 168–170 °C, was obtained in 78% yield. After recrystallization from isopropyl alcohol and heptane (2:1), 2 melted at 195–196 °C; NMR ($CDCl_3$) δ 6.55–8.70 (m, 7); IR (KBr) 3130 (ArC–H), 1690 (C=O), 1540 (NO_2 asymmetric), 1180–1125 (C–F), and 1330 cm^{-1} (NO_2 symmetric); mass spectrum *m/e* (rel intensity) 341 (17.3), 340 (100), 294 (59.6), 267 (14.4), 266 (97.6), 222 (13.6), 197 (13.9), 96 (23.8), 69 (24.9), and 45 (16.9).

Anal. Calcd for $C_{14}H_7F_3N_2O_3S$: C, 49.42; H, 2.07; F, 16.75; N, 8.23; S, 9.42. Found: C, 49.31; H, 2.06; F, 16.68; N, 8.15; S, 9.63.

2-(2,6-Dinitro-4-trifluoromethylphenylthio)benzimidazole (3). To a stirred solution containing 30 g (0.2 mol) of 2-mercaptobenzimidazole, 13.2 g (0.2 mol) of 85% potassium hydroxide, 200 ml of DMF, and 20 ml of water, 54 g (0.2 mol) of 4-chloro-3,5-dinitrobenzotrifluoride was added in one portion. An exothermic reaction set in causing a temperature rise from 25 to 47 °C. Immediately the reaction mixture was cooled to 30 °C and stirred at 25–30 °C for 4 days. After cooling to 10 °C, 800 g of ice water was added and stirring continued at 0–10 °C for 1 h. The solid was collected by filtration, washed with water until the washings were neutral to litmus, and air dried at

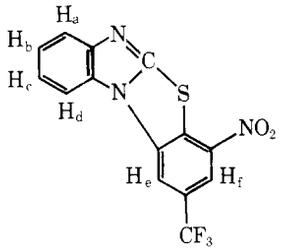
25–30 °C. The crude product, **3**, mp 247–249 °C, was obtained in 94% yield. After recrystallization from isopropyl alcohol **3** melted at 248–250 °C; NMR (Me_2SO-d_6) δ 6.90–7.60 (m, 4), 8.65 (s, 2); mass spectrum *m/e* (rel intensity) 384 (38), 338 (57), 292 (60), 274 (30), 251 (15), 223 (18), 133 (100), 106 (21), 102 (12), and 90 (23).

Anal. Calcd for $C_{14}H_7F_3N_4O_4S$: C, 43.76; H, 1.84; F, 14.83; N, 14.58; S, 8.38. Found: C, 43.85; H, 1.81; F, 14.70; N, 14.54; S, 8.57.

2-(2-Nitro-4-trifluoromethylphenylthio)benzimidazole (4). The procedure was identical with that described for product **3** except that 0.2 mol of 4-chloro-3-nitrobenzotrifluoride was substituted for the 4-chloro-3,5-dinitrobenzotrifluoride and the stirred reaction mixture was heated at 90–100 °C for 24 h. The crude product (**4**), mp 214–215 °C, was obtained in 95% yield. After recrystallization from methyl alcohol **4** melted at 218 °C; NMR (Me_2SO-d_6) δ 7.00–8.10 (m, 6), 8.45 (s, 1, $H_{3'}$); mass spectrum *m/e* (rel intensity) 339 (54.1), 294 (17.3), 293 (100), 292 (22.2), 206 (35.4), 133 (50.7), 122 (17.5), 106 (16.4), 90 (23.0), and 63 (21.0).

Anal. Calcd for $C_{14}H_8F_3N_3O_2S$: C, 49.56; H, 2.38; F, 16.80; N, 12.38; S, 9.45. Found: C, 49.50; H, 2.27; F, 17.06; N, 12.30; S, 9.50.

2-(Trifluoromethyl)-4-nitrobenzimidazo[2,1-*b*]benzothiazole (5). Method I. The charge and procedure were identical with those described for **3** except that after the addition of 4-chloro-3,5-dinitrobenzotrifluoride the stirred reaction mixture was heated at 90–100 °C for 24 h. During this heating period a brownish-yellow gas was liberated. The crude product, mp 26–269 ° C, was obtained in 86% yield. After recrystallization from DMF it melted at 275 °C; NMR (Me_2SO-d_6) below (sample was run on 90 MHz at ambient temperature with time averaging for 340 scans; a computer simulation was obtained of the four-spin system with assignments taken from the experimental spectrum); IR (CsI) 3090 (ArC–H), 1690–1480 (C=N), 1545(NO_2 asymmetric), 1400–1100 (C–F), 1295 (NO_2 symmetric), and 700–600 cm^{-1} (C–S); mass spectrum *m/e* (rel intensity) 337 (100), 318 (3), 291 (78), 279 (5), 271 (2), 247 (7), 227 (5), 222 (3), 178 (2), 168.5 (5), and 69 (7).



δ H_a 2143 Hz (8.7 ppm)	J_{ab} = +7 Hz
δ H_b 2038 Hz (7.5 ppm)	J_{bc} = +7 Hz
δ H_c 2028 Hz (7.4 ppm)	J_{cd} = +7 Hz
δ H_d 2062 Hz (7.8 ppm)	J_{ac} = +1.5 Hz
δ H_e 2168 Hz (8.9 ppm)	J_{bd} = +1.5 Hz
δ H_f 2134 Hz (8.6 ppm)	J_{ad} = 0

Method II. A stirred charge containing 19.2 g (0.05 mol) of **3** in 100 ml of DMf was heated at 90–100 °C for 24 h. During this heating period a brownish-yellow gas was liberated. After cooling to 30 °C, 400 ml of water was added and stirring continued for 1 h. The solid was collected by filtration, washed with water until the washings were neutral to litmus, and dried at 25–30 °C. The crude product, mp 272–274 °C, was obtained in 83% yield. After recrystallization from DMF it melted at 275 °C. A mixture melting point with the product obtained from method I was not depressed and the NMR and IR spectra of the two were superimposable.

Anal. Calcd. for $C_{14}H_6F_3N_3O_2S$: C, 49.86; H, 1.79; F, 16.90; N, 12.46; S, 9.51. Found: C, 49.94; H, 1.80; F, 16.73; N, 12.43; S, 9.46.

Attempted Cyclization of 4. A stirred mixture containing 34 g (0.1 mol) of **4** and 100 ml of dimethylformamide, *o*-dichlorobenzene, or nitrobenzene was heated at reflux temperatures for 24 h. During this heating period no gas was liberated and the solution became black. The first solvent furnished unchanged **4** and the latter two solvents afforded decomposed **4** (tars).

Registry No.—**1**, 60968-20-9; **2**, 60968-21-0; **3**, 60968-22-1; **4**, 60968-23-2; **5**, 60968-24-3; 2-benzothiazolol, 934-34-9; 4-chloro-3,5-dinitrobenzotrifluoride, 393-75-9; 4-chloro-3-nitrobenzotrifluoride, 121-17-5; 2-mercaptobenzimidazole, 583-39-1.

Supplementary Material Available. Mass spectral fragmentation routes for **3** and **5** (2 pages). Ordering information is given on any current masthead page.

References and Notes

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(4) (a) G. F. Buffin and J. D. Kendall, *J. Chem. Soc.*, 361 (1956); (b) J. A. Van Allan, *J. Org. Chem.*, **21**, 24 (1956); (c) J. J. D'Amico, R. H. Campbell, and E. C. Guinn, *ibid.*, **29**, 865 (1964).

Syntheses and Some Properties of 4-Acyl-1-methyl-2-azathiabenzene 1-Oxides

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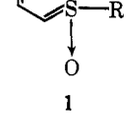
A series of 4-acyl-1-methyl-2-azathiabenzene 1-oxides have been prepared by base-catalyzed cyclization of *N*-(β,β-diacylvinyl)dimethylsulfoximines which, in turn, were obtained by the reactions of 3-ethoxymethylene-2,4-pentanedione, diethyl ethoxymethylenemalonate, ethyl 2-(ethoxymethylene)acetoacetate, and 2-acetyl-3-methoxy-2-cyclohexen-1-one with dimethylsulfoximine. Comparison of the physical and chemical properties of the azathiabenzene 1-oxides with those of the corresponding 4-acyl-1-methylthiabenzene 1-oxides suggests that both the ylidic and betainelike properties of the 2-azathiabenzene 1-oxides are much lower than those of the latter.

Thiabenzene 1-oxides (**1**) are of substantial intrinsic interest as heterocycles containing six π electrons in a cyclic conjugated ring system; if the 6π electrons can delocalize in the ring through sulfur, they are expected to be aromatic. Previous syntheses and studies of the properties of such 6π heterocycles,[1-5] however, have demonstrated that they can be best represented as cyclic ylidic structures.

The introduction of a heteroatom into the thiabenzene 1-oxides ring system is expected to alter significantly the electronic structure of **1**. Cram and Williams[6] have recently synthesized 3,5-diphenyl-1-methyl-2-azathiabenzene 1-oxide (**2**) and suggested that it is not aromatic on the basis of NMR



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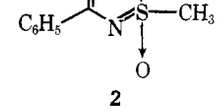

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