under a static nitrogen atmosphere with a gas bubbler. The mixture was heated to the temperature where nitrogen evolution was steady (typically 160–190 °C) until the gas evolution ceased (20 min–1.5 h). The mixture was cooled and the decalin was removed by kugelrohr distillation [50 °C (0.5 mm)]. The residue was triturated with methylene chloride twice and filtered to remove sulfur. The solution was then concentrated onto silica gel and chromatographed on the same with ether–hexane (typically 1% ether) to obtain in most cases the benzopentathiepin contaminated with sulfur. The product was further purified by recrystallization and/or medium- (Lobar, Silica gel 60 Size C, hexane) or high-pressure (Zorbax Sil, hexane) liquid chromatography. This procedure has been successfully carried out on a 0.25–10 g scale.

Benzopentathiepin: 35% without Dabco; 54% with Dabco; mp 58–60 °C (hexane) (lit.[5a] mp 65–66 °C); NMR δ 7.85–7.7 and 7.45–7.2 (AA'BB' m); mass spectrum, m/e 235.8914; calcd m/e for $C_6H_4S_5$, 235.8917.

7-Chlorobenzopentathiepin: 22% without Dabco; mp 87.5–89 °C (hexane); NMR δ 7.9–7.7 (d, 2 H), 7.4–7.2 (m, 1 H); IR (KBr) 1095, 822 cm^{-1}; mass spectrum, m/e 269.8517; m/e calcd for $C_6H_3ClS_5$, 269.8527.

Anal. Calcd for $C_6H_3ClS_5$: C, 26.61; H, 1.12. Found: C, 26.84; H, 1.22.

7-(Trifluoromethyl)benzopentathiepin: 31% without Dabco; mp 59–60 °C (hexane); NMR δ 8.18 (d, J = 2 Hz, 1 H), 8.0 (d, J = 8 Hz, 1 H), 7.55 (dd, J = 2, 8 Hz, 1 H); IR (KBr) 1320 cm^{-1}; mass spectrum, m/e 303.8788; calcd m/e for $C_7H_3F_3S_5$, 303.8790.

Anal. Calcd for $C_7H_3F_3S_5$: C, 27.62; H, 0.99. Found: C, 27.92; H, 0.94.

7-(Dimethylamino)benzopentathiepin: 45% without Dabco; may be isolated pure from the column chromatography; mp 121.5–122.5 °C (ethanol); NMR δ 7.55 (d, J = 8.5 Hz, 1 H), 7.0 (d, J = 2.7 Hz, 1 H), 6.5 (dd, J = 8.5, 2.7 Hz, 1 H), 3.0 (s, 6 H); IR (KBr) 1583 cm^{-1}; mass spectrum, m/e 278.9343; calcd m/e for $C_8H_9NS_5$, 278.9338.

Anal. Calcd for $C_8H_9NS_5$: C, 34.38; H, 3.25; S, 57.36. Found: C, 34.21; H, 3.42; S, 56.99.

7-Methoxybenzopentathiepin: 34% without Dabco; 57% with Dabco; may be isolated pure directly from the column chromatography; mp 97–98 °C; NMR δ 7.75 (d, J = 8.3 Hz, 1 H), 7.3 (d, J = 2.7 Hz, 1 H), 6.8 (dd, J = 2.7, 8.3 Hz, 1 H), 3.85 (s, 3 H); mass spectrum, m/e 265.9011; m/e calcd for $C_7H_6OS_5$, 265.9022.

6-Bromobenzopentathiepin: 14% without Dabco; 22% with Dabco; mp 101–101.5 °C (hexane); NMR (360 MHz) δ 7.78 (dd, J = 1.3, 8.0 Hz, 1 H), 7.66 (dd, J = 1.3, 8.0 Hz, 1 H), 7.2 (t, J = 8.0 Hz, 1 H); IR (KBr) 788 cm^{-1}.

Anal. Calcd for $C_6H_3BrS_5$: C, 22.86; H, 0.96. Found: C, 23.09; H, 0.94.

6-(Trifluoromethyl)benzopentathiepin: 20% without Dabco; mp 61–62 °C (hexane); NMR δ 8.1 (long range coupled d, J = 8.0 Hz, 1 H), 7.85 (long range coupled d, J = 8.0 Hz, 1 H), 7.48 (long range coupled t, J = 8.0 Hz, 1 H).

Anal. Calcd for $C_7H_3F_3S_5$: C, 27.62; H, 0.99. Found: C, 27.65; H, 1.03.

Registry No. 1 (R = H), 17071-97-5; 1 (R = 7-Cl), 88888-94-2; 1 (R = 7-CF_3), 88888-95-3; 1 (R = 7-MeO), 88888-96-4; 1 (R = 7-Me_2N), 88888-97-5; 1 (R = 6-Br), 88888-98-6; 1 (R = 6-CF_3), 88888-99-7; $CF_3C(O)ONa$, 2923-18-4; Na_2S, 1313-82-2; S_8, 7704-34-9; Dabco, 280-57-9; 4-bromo-1,2,3-benzothiadiazole, 31860-00-1; 2-chloro-4-(trifluoromethyl)nitrobenzene, 402-11-9; 1-(trifluoromethyl)-3-mercapto-4-hydrazinobenzene hydrochloride, 88888-90-8; 1,2,3-benzothiadiazole, 273-77-8; 6-chloro-1,2,3-benzothiadiazole, 23644-01-1; 6-(trifluoromethyl)-1,2,3-benzothiadiazole, 88888-91-9; 5-methoxy-1,2,3-benzothiadiazole, 31860-05-6; 5-(dimethylamino)-1,2,3-benzothiadiazole, 88888-92-0; 4-(trifluoromethyl)-1,2,3-benzothiadiazole, 88888-93-1.

Pyrazolothiadiazoles from 3-Aminopyrazoles: The Hetero-Herz Reaction

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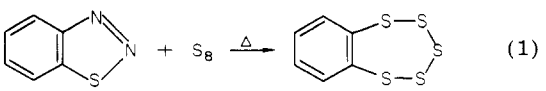
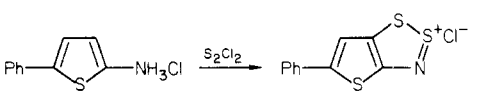
The reaction of sulfur monochloride with pyrazoleamines gives good to excellent yields of pyrazolodithiazolium chlorides from a hetero-Herz reaction. No chlorination of the pyrazole nucleus was observed—a normal occurrence in Herz reactions. The Herz salts were converted to novel pyrazolothiadiazoles.

We recently discovered a new reaction of 1,2,3-benzothiadiazoles with sulfur (eq 1) that results in the direct formation of benzopentathiepins.[1] To explore the scope



(1)

of this reaction, we required access to hetero-fused 1,2,3-thiadiazoles. The usual preparation of fused 1,2,3-thiadiazoles is by diazotization of *o*-amino thiols.[2] These thiols are available from *o*-chloronitrobenzenes, benzothiazoles, or by the Herz reaction[3] of anilines with sulfur monochloride. We perceived that heterocyclic amines would be the most easily accessible precursors and therefore we chose to examine the hetero-Herz reaction. While the Herz reaction with anilines has been extensively explored,[4] there has been surprisingly little work on its use with heterocyclic amines. There is one report on the preparation of a thiophene Herz salt (eq 2).[5] We report here the preparation of a series of 5-substituted 3-aminopyrazoles, their efficient conversion to pyrazolodithiazolium chlorides via the Herz reaction, and the preparation of novel pyrazolo-



(2)

† Contribution No. 3368 from the department.

(1) Chenard, B. L.; Miller, T. J. *J. Org. Chem.*, preceding paper in this issue.
(2) For an excellent review of benzothiadiazole synthesis, see: Lionel, G. D., Ph.D. Dissertation, Cornell University, 1973.
(3) L. Cassella and Co.; German Patents 360 690, 364 822, 367 344, 367 345, 367 346, 370 845.
(4) Warburton, W. K. *Chem. Rev.* **1957**, 1011–1120.
(5) Abramenko, P. I.; Ponomareva, T. K.; Priklonskikh, G. I. *Khim. Geterotsikl. Soedin.* **1979**, *4*, 477–480.

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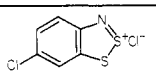
Table I. UV Spectra for Herz Salts in Trifluoroacetic Acid

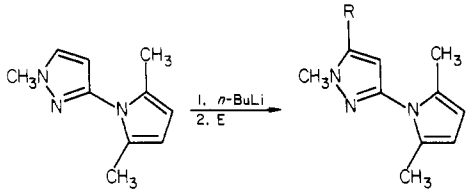
compound	color	λ_{max}, nm (ϵ)	ref
	yellow-brown	417 (3980) 366 (12590)	10
5a	orange	452 (1590) 326 (10200)	*a*
5b	red	500 (1180) 328 (8660)	*a*
5d	yellow	442 (1470) 328 (8100)	*a*

[a] Present work.

thiadiazoles from these salts.

Results and Discussion

Pyrazole Synthesis. 1-Methyl-3-aminopyrazole (1) is available in quantity by the published procedure.[6] Several attempts to introduce functionality directly onto C-5 of 1 were unsuccessful. The recent report[7] of the use of the 2,5-dimethylpyrrole unit as an effective protecting group for aromatic and heteroaromatic amines led us to examine its use with pyrazole amines. 3-(2,5-Dimethylpyrrolyl)-1-methylpyrazole (2)[8] was prepared from 1 and acetonylacetone by azeotropic removal of water. Metalation of 2 with *n*-butyllithium proceeded smoothly in THF at −78 °C to generate the 5-lithio species, which was quenched with several electrophiles to give **3a–d** in good yield. With

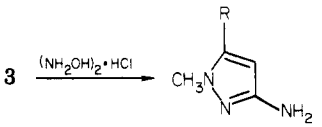


2

3a, R = Cl (50%)
b, R = Br (76%)
c, R = CO_2CH_3 (64%)
d, R = $CO_2C_2H_5$ (60%)

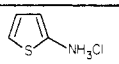
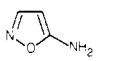
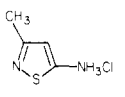
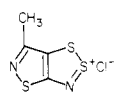
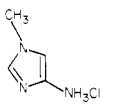
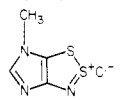
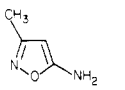
both cyanogen bromide and chloride, only the halogen was transferred. When a chloroformate was the electrophile, it was important to maintain the low temperature and to employ an excess of the electrophile to minimize addition of a second molecule of anion to the product ester.

Removal of the pyrrole protecting group was not effected by hydroxylamine hydrochloride as reported.[7] However, an earlier paper[9] described the use of hydroxylamine hemichloride to hydrolyze pyrroles to bis oximes of succindialdehyde. This reagent, generated in situ, effectively hydrolyzed the 2,5-dimethylpyrrolyl group, affording the desired amines **4b–d** in good yield. We observed no interference from either the pyrazole ring or the esters (**3c,d**) in the hydrolysis.



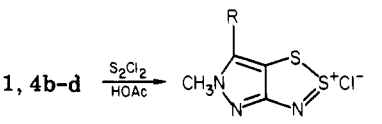
4b, R = Br (86%)
c, R = CO_2CH_3 (81%)
d, R = $CO_2C_2H_5$ (90%)

Table II. Herz Reaction with Other Heterocyclic Amines

entry	amine	product (% yield)	λ_{max}, nm (ϵ)[a]
1		tar	
2		tar	
3		 (68)[b]	434 (110) 277 (16600)
4		 (56)[b]	382 (3490)
5		tar	

[a] UV taken in trifluoroacetic acid. [b] Structural assignment is tentative (see text).

Hetero-Herz Reaction. The amines 1 and **4b–d** were dissolved in glacial acetic acid and added to ice-cold sulfur monochloride. The mixtures became intensely colored and were then warmed to 40–65 °C. For **4c,d** it was critical that the medium be maintained below 45 °C as the product decomposed at higher temperature. After 1–4 h, the mixtures were cooled to ambient temperature and diluted with benzene to precipitate the Herz salt. The highly colored, moisture-sensitive compounds were filtered under nitrogen, washed well with dry benzene, and dried in a stream of nitrogen to afford good yields of **5a–d**.



5a, R = H (93%)
b, R = Br (74%)
c, R = CO_2CH_3 (65%)
d, R = $CO_2C_2H_5$ (45%)

Structure proof for **5a–d** rests on the UV spectra taken in trifluoroacetic acid (Table I) and conversion to their corresponding pyrazolothiadiazoles. The UV spectra showed two bands, one of which was very sensitive to the 6-substituent. These spectra are similar to those reported[10] for Herz salts of aniline derivatives and indicate a similar chromophore.

The Herz reaction might be expected to proceed well for 3-aminopyrazoles since the 4-position is known to be the preferred site of electrophilic attack[11] even in the absence of the amino group. We were surprised, however, that the carboalkoxy group (**4c,d**) did not interfere with the process since it could have reduced the electrophilicity of C-4.

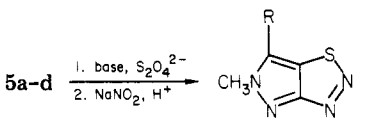
Nuclear chlorination nearly always occurs in the Herz reaction. Substitution of a variety of groups including H, NO_2, and CO_2H has been observed from both the ortho and para positions in aniline derivatives.[4,12] Based on

(6) Ege, G.; Arnol, P. *Synthesis* **1976**, 52.
(7) Breukelman, S. P.; Meakins, G. D.; Tirel, M. D. *J. Chem. Soc., Chem. Commun.* **1982**, 800–801.
(8) Hori, I.; Igarashi, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2856–2858.
(9) Findley, S. P. *J. Org. Chem.* **1956**, *21*, 644.
(10) Huestis, L. D.; Walsh, M. L.; Hahn, N. *J. Org. Chem.* **1965**, *30*, 2763–2766.
(11) Paquette, L. A. "Modern Heterocyclic Chemistry"; W. A. Benjamin: New York, 1968; pp 194–199.
(12) Kirby, P.; Soloway, S. B.; Davies, J. H.; Webb, S. B. *J. Chem. Soc. C* **1970**, 2250–2253.

these observations, we had hoped that the Herz reaction with 1 might lead directly to the chlorinated **5**. However, we found no evidence for chlorination with our reaction conditions.

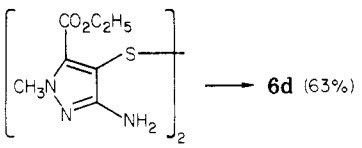
We have further examined the scope of this hetero-Herz reaction with other heterocyclic amines and their hydrochloride salts. Table II lists several of the amines that we examined. In no case did we enjoy the success of the Herz reaction which we achieved with the pyrazoles. In some experiments (entries 3, 4) we obtained products that gave UV spectra consistent with a dithiazolium chloride; but, since we were unable to convert these products to more than trace amounts of hetero-fused thiadiazoles, the assignment of structure must remain tentative at best. Notable was the failure to obtain a characterizable product in the case of 2-aminothiophene hydrochloride (entry 1) in light of the successful Herz reaction noted in eq 2. A possible explanation for this failure may be the additional electrophilic site available at C-5 which makes polymerization plausible.

Pyrazolothiadiazoles. The dithiazolium chlorides **5a,b** were conveniently hydrolyzed and reduced in an open Erlenmeyer flask with an aqueous solution of potassium hydroxide and sodium dithionite by brief warming to 90 °C. The resulting clear solutions were treated with sodium nitrite and acidified (see Experimental Section) to give the desired pyrazolothiadiazoles **6a,b** in 37% and 44% yields, respectively.



6a, R = H (37%)
b, R = Br (44%)
c, R = CO_2CH_3 (27%)
d, R = $CO_2C_2H_5$ (53%)

With the esters **5c,d**, aqueous carbonate was the base of choice for the hydrolysis since potassium hydroxide caused significant hydrolysis of the ester group. A problem with this reaction is that significant amounts of disulfide **7** are formed even when the reaction is carried out under an inert atmosphere. This disulfide could be filtered from



7

the aqueous solution prior to diazotization. While this was an inconvenience, it was later observed that **7** also gave **6d** (63%) on diazotization. The similar conversion of *o*-aminobenzenethiol disulfides to benzothiadiazoles has been previously described.[13]

The conversion of the pyrazolodithiazolium chlorides **5a–d** to their corresponding pyrazolothiadiazoles **6a–d** thus establishes the successful application of the Herz reaction to pyrazoles. The pyrazolothiadiazoles represent a new heterocyclic ring system. The chemistry of these compounds is under active investigation in our laboratory.

Experimental Section

General Procedures. Melting points were taken with a Thomas Hoover or a Buchi capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Nicolet 7199 FT infrared spectrometer and are reported in reciprocal centimeters. Only strong bands are reported unless otherwise stated. Routine proton NMR were obtained at either 80 or 90 MHz with a Varian EM390 or an IBM NR80 FT instrument. NMR data are reported in parts per million (δ) downfield from tetramethylsilane in deuteriochloroform. Analyses were determined by either Micro-Analysis, Inc., Wilmington, DE, or Galbraith Laboratories, Inc., Knoxville, TN. Dry THF was stored under nitrogen over a sodium chip. *n*-Butyllithium (1.6 M) was from Foote Mineral Co. and was used without titration.

5-Bromo-3-(2,5-dimethylpyrrolyl)-1-methylpyrazole (3b). A solution of 3-(2,5-dimethylpyrrolyl)-1-methylpyrazole (2.0 g, 11.4 mmol) and dry tetrahydrofuran (100 mL) was cooled to −78 °C, and *n*-butyllithium (7.8 mL, 1.6 M, 12.48 mmol) was added over 3 min. The solution was stirred 1.5 h at −78 °C, and then a solution of cyanogen bromide (1.3 g, 12.5 mmol) in tetrahydrofuran (3 mL) over a spatula of sodium sulfate (to dry the BrCN) was taken up away from the drying agent and syringed into the reaction. The mixture was warmed to ambient temperature, the solvent was removed at reduced pressure, and the residue was partitioned between ether and water. The phases were separated, and the organic layer was washed with brine, filtered through a cone of sodium sulfate, and concentrated. The residue was chromatographed on silica gel (200 g, 25% ether–hexane) to give 2.22 g, 76%, of 5-bromo-3-(2,5-dimethylpyrrolyl)-1-methylpyrazole as a white solid: mp 66–69 °C; IR (KBr) 1528 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.2 (s, 1 H), 5.83 (s, 2 H), 3.88 (s, 3 H), 2.1 (s, 6 H). An analytical sample was sublimed at 55 °C (0.3 mm).

Anal. Calcd for $C_{10}H_{12}BrN_3$: C, 47.26; H, 4.76; N, 16.53. Found: C, 46.96; H, 4.66; N, 16.28.

5-Chloro-3-(2,5-dimethylpyrrolyl)-1-methylpyrazole (3a) was prepared according to the procedure of **3b**: colorless solid, 50%; mp 59–61 °C; ^1H NMR ($CDCl_3$) δ 6.1 (s, 1 H), 5.84 (s, 2 H), 3.84 (s, 3 H), 2.1 (s, 6 H); IR (KBr) 1529 cm^{-1}. A sample sublimed at 50 °C (0.3 mm) had mp 60–63 °C.

Anal. Calcd for $C_{10}H_{12}ClN_3$: C, 57.28; H, 5.77; N, 20.04. Found: C, 57.00; H, 5.82; N, 19.81.

5-Carbethoxy-3-(2,5-dimethylpyrrolyl)-1-methylpyrazole (3d). A solution of 3-(2,5-dimethylpyrrolyl)-1-methylpyrazole (5.0 g, 28.6 mmol) in dry tetrahydrofuran (250 mL) was cooled to −78 °C. *n*-Butyllithium (19.5 mL, 1.6 M, 31.2 mmol) was added dropwise over 15 min followed by stirring 2 h at −78 to −60 °C. Ethyl chloroformate (3.58 mL, 37.5 mmol) was added and the solution was warmed to room temperature and stirred 1 h. The solvent was removed at reduced pressure and the residue was partitioned between ether and water. Phases were separated and the organic layer was washed with brine, filtered through a cone of sodium sulfate, and concentrated to leave an oil. This residue was chromatographed on silica gel (600 g, 15% ether–hexane) to give, after an 850-mL forerun, 0.18 g of an impurity in 500 mL and 4.69 g of oil in 700 mL. The oil was Kugelrohr distilled at 100–110 °C (0.15 mm) to give 4.24 g, 60%, of 5-carbethoxy-3-(2,5-dimethylpyrrolyl)-1-methylpyrazole as a clear oil: IR (neat) 1728, 1546, 1494, 1273, 1252 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.78 (s, 1 H), 5.9 (s, 2 H), 4.38 (q, 2 H), 4.21 (s, 3 H), 2.1 (s, 6 H), 1.4 (t, 3 H).

Anal. Calcd for $C_{13}H_{17}N_3O_2$: C, 63.14; H, 6.93; N, 16.99. Found: C, 62.83; H, 6.93; N, 16.67.

5-Carbomethoxy-3-(2,5-dimethylpyrrolyl)-1-methylpyrazole (3c) was prepared according to the procedure of **3d**: white solid; 64%; mp 63–65 °C; ^1H NMR ($CDCl_3$) δ 6.7 (s, 1 H), 5.8 (s, 2 H), 4.2 (s, 3 H), 3.85 (s, 3 H), 2.1 (s, 6 H).

5-Bromo-3-amino-1-methylpyrazole (4b). A solution of potassium hydroxide (0.4 g, 7.15 mmol) in water (6 mL) and ethanol (6 mL) was added to a slurry of hydroxylamine hydrochloride (0.94 g, 14.3 mmol) in ethanol (10 mL). 5-Bromo-3-(2,5-dimethylpyrrolyl)-1-methylpyrazole (0.72 g, 2.84 mmol) was added and the mixture was refluxed 60 h. The solvents were removed at reduced pressure and the residue was triturated with ether. Sodium sulfate was added and the heterogeneous mixture was filtered. The solvent was evaporated from the filtrate, and the residue was chromatographed on silica gel (100 g, ethyl acetate–hexane gradient) to give 0.43 g, 86%, of 5-bromo-3-amino-1-methylpyrazole as an off-white solid: mp 53–55 °C; ^1H

(13) (a) Montevecchi, P. C.; Tundo, A. *J. Org. Chem.* **1981**, *46*, 4998–4999. (b) Ward, E. F.; Heard, D. D. *J. Chem. Soc.* **1965**, 1023–1028.

NMR ($CDCl_3$) δ 5.63 (s, 1 H), 3.68 (s, 3 H), 3.9–3.4 (br s, 2 H); IR (KBr) 3388, 3310, 1548, 1484, 750 cm^{-1}. A sample sublimed at 30 °C (0.18 mm) had mp 54–56 °C.

Anal. Calcd for $C_4H_6BrN_3$: C, 27.30; H, 3.44; N, 23.87. Found: C, 27.27; H, 3.43; N, 23.59.

5-Carbomethoxy-3-amino-1-methylpyrazole (4c) was prepared according to the procedure of **4b**: white solid; 81%; mp 114–118 °C; ^1H NMR ($CDCl_3$) δ 6.17 (s, 1 H), 4.02 (s, 3 H), 3.88 (s, 1 H), 3.7 (br s, 2 H); IR (KBr) 1719, 1551, 1263, 1102, 756 cm^{-1}; mass spectrum, m/e 155.0682, m/e calcd for $C_6H_9N_3O_2$ 155.0694.

5-Carbethoxy-3-amino-1-methylpyrazole (4d) was prepared according to the procedure of **4b**: off-white solid; 90%; mp 57–58 °C; IR (KBr) 3420, 1720, 1550, 1488, 1268, 1102 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.14 (s, 1 H), 4.31 (q, 2 H), 3.97 (s, 3 H), 3.4 (br s, 2 H), 1.33 (t, 3 H). A sample sublimed at 35 °C (0.15 mm) had mp 58–60 °C.

Anal. Calcd for $C_7H_{11}N_3O_2$: C, 49.70; H, 6.55; N, 24.84. Found: C, 49.72; H, 6.43; N, 24.57.

5-Methylpyrazolodithiazolium Chloride (5a). Sulfur monochloride (100 mL) was cooled to 0 °C, and 3-amino-1-methylpyrazole (17.48 g, 180 mmol) in acetic acid (28 mL) was added dropwise over 10 min. The resulting mixture was warmed to ambient temperature; then it was gradually heated to 65 °C over 3 h and maintained at 65 °C for 2 h. The mixture was cooled and benzene (240 mL) was added. The precipitate was filtered under nitrogen and rinsed with benzene to give 32.5 g, 93%, of 5-methylpyrazolodithiazolium chloride as a bright orange solid: IR (KBr) 1646, 1116, 712 cm^{-1}; UV (trifluoroacetic acid) 452 nm (1590), 326 (10200); mp, decomposed above 190 °C.

6-Bromo-5-methylpyrazolodithiazolium chloride (5b) was prepared according to the procedure of **5a**: red solid; 74%; mp 200 °C dec; UV (trifluoroacetic acid) 500 nm (1180), 328 (8660).

6-Carbethoxy-5-methylpyrazolodithiazolium Chloride (5c). Sulfur monochloride (3.3 mL) was chilled to 0 °C and 5-carbethoxy-3-amino-1-methylpyrazole (1.0 g, 5.9 mmol) in acetic acid (1.3 mL) was added dropwise over 5 min. The mixture was warmed to 40 °C and stirred at this temperature for 4 h. The mixture was cooled and diluted with benzene (20 mL); then it was filtered under nitrogen and rinsed with three portions of benzene. The yellow solid was dried under a stream of nitrogen to give 0.7 g, 45%, of 6-carbethoxy-5-methylpyrazolodithiazolium chloride as a bright yellow solid: mp 98 °C dec; UV (trifluoroacetic acid) 442 nm (1470), 328 (8100).

6-Carbomethoxy-5-methylpyrazolodithiazolium chloride (5d) was prepared according to the procedure of **5c**: bright yellow solid; 65%.

5-Methylpyrazolo-1,2,3-thiadiazole (6a). 5-Methylpyrazolodithiazolium chloride (30 g, 0.155 mol) was added all at once to a solution of 5% potassium hydroxide (500 mL) and sodium hydrosulfite (30 g, 0.172 mol). The resulting mixture was heated to 90 °C for 1 h; then it was cooled. Sodium nitrite (15 g, 0.217 mol) was dissolved in the clear light brown solution, and it was added dropwise to 5% aqueous H_2SO_4 (600 mL) over 1.5 h. The mixture was stirred 20 min more; then it was brought to pH 9 with 20% aqueous NaOH and stirred overnight. The precipitate was filtered, rinsed with water, and air-dried to give 7.45 g of product, mp 110–119 °C. The filtrate was extracted with methylene chloride. Concentration of this extract gave another 4.54 g of product. The combined product was sublimed at 80 °C (0.3 mm) to give 8.14 g (37.5%) of 5-methylpyrazolo-1,2,3-thiadiazole as a colorless solid. A sample recrystallized from methylene chloride–hexane had mp 125–127 °C: ^1H NMR ($CDCl_3$) δ 7.7 (s, 1 H), 4.25 (s, 3 H); IR (KBr) 1289 cm^{-1}.

Anal. Calcd for $C_4H_4N_4S$: C, 34.28; H, 2.88; N, 39.97. Found: C, 34.24; H, 2.98; N, 40.15.

6-Bromo-5-methylpyrazolo-1,2,3-thiadiazole (6b) was prepared according to the procedure of **6a**: colorless solid; 44%; mp 99–101 °C; ^1H NMR ($CDCl_3$) δ 4.2 (s, 3 H); IR (KBr) 1308, 1275, 669 cm^{-1}; mass spectrum, m/e 217.9263, m/e calcd for $C_4H_3BrN_4S$ 217.9262.

Anal. Calcd for $C_4H_3BrN_4S$: C, 21.93; H, 1.38. Found: C, 21.97; H, 1.54.

6-Carbethoxy-5-methylpyrazolo-1,2,3-thiadiazole (6d). 6-Carbethoxy-5-methylpyrazolodithiazolium chloride (1.0 g, 3.77 mmol) was added to a solution of sodium hydrosulfite (1.2 g) in 5% aqueous sodium bicarbonate (25 mL) under a nitrogen atmosphere. The mixture was heated to 95 °C for 25 min; then it was cooled and gravity filtered to give a bright yellow solid, 5-carbethoxy-4-mercapto-3-amino-1-methylpyrazole disulfide (**7**) (mp 149–150.5 °C). Sodium nitrite (0.6 g) was dissolved in the filtrate, which was then added dropwise to 5% aqueous sulfuric acid (50 mL). The mixture was stirred for 3 h followed by careful neutralization to pH 7 with solid sodium carbonate. The mixture was extracted with methylene chloride. The organic phase was washed with brine; then it was filtered through a cone of sodium sulfate and concentrated to leave 0.43 g, 53%, of 6-carbethoxy-5-methylpyrazolo-1,2,3-thiadiazole as an off-white solid: mp 91–94 °C; ^1H NMR ($CDCl_3$) δ 4.55 (s, 3 H), 4.45 (q, J = 6.9 Hz, 2 H), 1.4 (t, J = 6.9 Hz, 3 H). A sample recrystallized from ether–hexane had mp 94.5–96 °C.

Anal. Calcd for $C_7H_8N_4O_2S$: C, 39.62; H, 3.80. Found: C, 39.99; H, 3.68.

6-Carbomethoxy-5-methylpyrazolo-1,2,3-thiadiazole (6c) was prepared according to the procedure for **6d**: white solid; 27%; mp 115–121 °C; ^1H NMR ($CDCl_3$) δ 4.57 (s, 3 H), 4.02 (s, 3 H); IR (KBr) 1736, 1443, 1272 cm^{-1}; mass spectrum, m/e 198.0204, m/e calcd for $C_6H_6N_4O_2S$ 198.0211.

6d from 3-Amino-5-carbethoxy-1-methylpyrazole-4-thiol Disulfide (7). A solution of **7** (0.65 g, 1.6 mmol) in water (16 mL) and concentrated HCl (9 mL) was chilled to 5 °C. Sodium nitrite (0.25 g, 3.6 mmol) in water (10 mL) was added dropwise over 15 min. After being stirred 30 min more, the mixture was carefully neutralized to pH 8 with solid potassium carbonate (ice cooling). The mixture was extracted with methylene chloride (3 × 30 mL). The combined organic phase was washed with brine, filtered through a cone of sodium sulfate, and concentrated. The residue was chromatographed on silica gel (60 g, methylene chloride eluent) to give 0.43 g (63%) of **6d** as the first component off the column. This product was identical with that prepared by the previous reaction.

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Registry No. **3a**, 89088-52-8; **3b**, 89088-51-7; **3c**, 89088-54-0; **3d**, 89088-53-9; **4b**, 89088-55-1; **4c**, 89088-56-2; **4d**, 89088-57-3; **5a**, 89088-58-4; **5b**, 89088-59-5; **5c**, 89088-60-8; **5d**, 89088-61-9; **6a**, 89088-62-0; **6b**, 89088-63-1; **6c**, 89088-65-3; **6d**, 89088-64-2; **7**, 89088-66-4; S_2Cl_2, 10025-67-9; 3-amino-1-methypyrazole, 1904-31-0; 3-(2,5-dimethylpyrrolyl)-1-methylpyrazole, 34605-66-8; 6-methylthiazolo[5,4-*d*]-1,2,3-dithiazolium chloride, 89088-67-5; 6-methylimidazo[5,4-*d*]-1,2,3-dithiazolium chloride, 89088-68-6; 5-amino-3-methylisothiazole hydrochloride, 71134-43-5; 4-amino-1-methylimidazole hydrochloride, 89088-69-7; 2-aminothiophene hydrochloride, 18621-53-9; 5-aminoisoxazole, 14678-05-8; 5-amino-3-methylisoxazole, 14678-02-5.