(m, 4 H). IR (KBr) 1310, 1480 cm^{-1}.

***cis*-1-(9-Anthryl)-2-nitroethylene (2).** A solution of **1** (250 mg; 1 mmol) in benzene (150 mL) under argon at 20 °C was irradiated for 1 h with a high-pressure mercury lamp (Philips HPK 125 W) in an immersion well apparatus equipped with a 400-nm cutoff filter solution (75 g of potassium nitrite in 100 mL of water; 1-cm path length). Workup by vacuum evaporation of solvent, followed by flash chromatography on silica gel/toluene and recrystallization from methylene chloride gave 210 mg (84%) of orange-red crystals: mp 187–192 °C (upon melting, **2** isomerizes to give **1**); ^1H NMR ($CDCl_3$) δ 8.50 (s, H-10), 8.06-8.01 (m, 2 H), 7.93–7.89 (m, 2 H), 7.70 (d, J = 9 Hz, 1 H), 7.61 (d, J = 9 Hz, 1 H), 7.53–7.46 (m, 4 H). Anal. Calcd for $C_{16}H_{11}NO_2$: C, 77.09; H, 4.45; N, 5.62. Found: C, 77.08; H, 4.49; N, 5.60; IR (KBr) 1340, 1500 cm^{-1}.

Photochemical Dimerization of 1 To Give 3–5. A solution of **1** (410 mg, 1.64 mmol) in methylene chloride (4 mL), placed in a cylindrical quartz cell of 1-cm path length and degassed by three freeze–thaw cycles, was irradiated for 6 h with a 1000-W xenon/mercury lamp in optical bench arrangement equipped with an Oriel LP 480 filter (cutoff at 435 nm). Partly, the dimers precipitated during the irradiation. According to ^1H NMR analysis, the reaction mixture consisted of starting material **1** (12%), its cis-isomer **2** (3%), Diels–Alder dimer **3** (56%), C_2-symmetrical dimer **4** (17%), and centrosymmetrical dimer **5** (12%). By addition of hexane, 50 mg of centrosymmetrical dimer **5** precipitated from the reaction mixture. It was washed with boiling methylene chloride (10 mL) to give 27 mg (7%) of **5** as colorless crystalline residue, melting with decomposition at 255–263 °C.

The solid residue obtained on vacuum evaporation of solvent from the original filtrate was washed with ether (5–10 mL) in order to dissolve **1** and **2**. From the residue, 191 mg (47%) of **3** and 25 mg (6%) of **4** were obtained by fractional crystallization from methylene chloride/hexane. The Diels–Alder dimer **3** forms lemon-yellow crystals, which melt with decomposition around 190 °C. The C_2-symmetrical dimer **4** forms colorless crystals, which decompose upon melting between 242 and 245 °C.

3: high-resolution mass spectrum, m/z calcd for $C_{32}H_{22}N_2O_4$ 498.15806, found 498.1583; IR (KBr) 1340, 1520, 1540 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.46 (s, H-10), 8.07–6.73 (m, 15 Ar H), 7.62 (obscured d, J = 14.3 Hz, 1 ethylenic H), 6.82 (d, J = 14.3 Hz, 1 ethylenic H), 5.94 (d, J = 9.2 Hz, 1 Ar H), 5.88 (dd, J = 6.9, 2.5 Hz, 1), 5.64 (d, J = 6.9 Hz, 1), 5.32 (d, J = 2.5 Hz, 1).[20] Anal. Calcd for $C_{32}H_{22}N_2O_4$: C, 77.10; H, 4.45. Found, C, 76.94; H, 4.40.

4: high-resolution mass spectrum, m/z calcd for $C_{32}H_{22}N_2O_4$ 498.15806, found 498.1578; IR (KBr) 1340, 1540 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.39–7.02 (m, 8), 6.39, (d, J = 10.4 Hz, H-2), 5.56 (d, J = 10.4 Hz, H-3), 4.84 (s, H-1). Anal. Calcd for $C_{32}H_{22}N_2O_4$: C, 77.10; H, 4.45; N, 5.62. Found, C, 77.10; H, 5.04; N, 5.22.

5: high-resolution mass spectrum, m/z calcd for $C_{32}H_{22}N_2O_4$ 498.15806, found 498.1590; IR (KBr) 1340, 1530 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.58–7.12 (m, 8), 5.72 (dd, J = 11.2, 2.3 Hz, H-2), 5.40 (d, J = 11.2 Hz, H-3), 4.84 (d, J = 2.3 Hz, H-1). Anal. Calcd for $C_{32}H_{22}N_2O_4$: C, 77.10; H, 4.45; N, 5.62. Found, C, 76.88; H, 4.40; N, 5.44.

Sodium Borohydride Reduction of Dimer 3 To Give 6. Sodium borohydride (20 mg, 0.53 mmol) was added to a stirred solution of **3** (125 mg, 0.25 mmol) in a mixture of methylene chloride (5 mL) and methanol (5 mL). After 10 min, when the yellow color of the solution had faded, the methylene chloride was removed by vacuum evaporation, and the remaining reaction mixture was diluted with water (10 mL) and extracted with five 25-mL portions of ether. The ether solution was dried over magnesium sulfate, and the residue obtained on vacuum evaporation of solvent was purified by flash chromatography on silica gel/toluene to give an oily substance, which gave pale yellow crystals upon addition of ether: yield, 90 mg (72%); mp 200–202 °C; ^1H NMR ($CDCl_3$) δ 8.42 (s, H-10), 8.22-6.71 (m, 15), 5.96 (d, J = 9.1 Hz, 1 Ar H), 5.79 (dd, J = 7.1, 2.3 Hz, 1), 5.46 (d, J = 7.1 Hz, 1), 5.21 (d, J = 2.3 Hz, 1), 4.44 (br m, 1), 4.24 (br m, 1), 3.11–2.97 (m, 1), 2.84–2.70 (m, 1). Anal. Calcd for $C_{32}H_{24}N_2O_4$: C, 76.79; H, 4.83; N, 5.60. Found: C, 77.19; H, 4.81; N, 5.33. High-resolution mass spectrum, m/z calcd for $C_{32}H_{24}N_2O_4$ 500.1736, found 500.1705; IR (KBr) 1350, 1530 cm^{-1}.

Thermolysis of 3 in Toluene. A solution of **3** (8 mg) in toluene (5 mL) was refluxed for 2 h. The residue obtained on vacuum evaporation of solvent was dissolved in deuterated chloroform and analyzed by ^1H NMR.

Registry No. **1**, 55446-60-1; **2**, 102781-65-7; **3**, 102781-66-8; **4**, 102781-67-9; **5**, 102850-00-0; **6**, 102781-68-0; 9-anthraldehyde, 642-31-9; nitromethane, 75-52-5.

(20) The doublet at 5.64 ppm is attributed to the methine proton adjacent to the 9-anthryl substituent in **3**. The corresponding signal in the ^1H NMR spectrum of compound **6** appears at 5.46 ppm. The remarkable downfield position most likely is due to deshielding by the adjacent nitro group. In the ^1H NMR spectrum of the Diels–Alder dimer of *trans*-1-(9-anthryl)-2-phenylethylene[14] the corresponding proton gives rise to a doublet at 4.92 ppm.

The Cine-Substitution Reaction of 5-Bromopyrimidines by Lithium Reagents

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In the 1970s we reported a useful synthetic transformation of 5-bromo-4-(methylthio)pyrimidines **1** (Scheme I; R^1 = H, OMe, SMe, NMe_2; R^2 = SMe) into 4,5′-bipyrimidines **7** upon treatment with 0.5 equiv of *n*-BuLi.[1] The reaction has been applied in the preparation of a series of biologically important, [(dimethylamino)ethyl]thio-substituted 4,5′-bipyrimidines.[2] The mechanism of this transformation was only briefly investigated, and, since quenching of the reaction mixture of **1b** with D_2O produced 5-deuterio-2,2′,4′,6-tetrakis(methylthio)-4,5′-bipyrimidine (**7b**), it was suggested (erroneously) that the respective 5-lithio derivative **2b** was the intermediate product[1a] in this cine-substituted reaction of the bromine atom. As an extension of our studies on this transformation we investigated the reactions of two closely related pyrimidines **1a** and **1b** with lithium reagents. We present evidence that the cine-substitution reaction of 4-(alkylthio)-5-bromopyrimidines involves a σ-adduct, such as **3**, between the 5-bromopyrimidine and a lithium compound.

Treatment of 5-bromo-2-(methylthio)pyrimidine (**1a**) in THF with 1 equiv of *n*-BuLi at −80 °C resulted in a bromine–lithium exchange reaction, because on quenching with D_2O, 5-deuterio-2-(methylthio)pyrimidine[3] was obtained as a sole product. When 0.5 equiv of *n*-BuLi was used and the reaction mixture was allowed to warm up to −20 °C and then quenched with water, another major compound was formed in a 72% yield. The product was air stable and had the empirical formula $C_{10}H_{11}BrN_4S_2$. It was positively identified as 5-bromo-2,2′-bis(methylthio)-3,4-dihydro-4,5′-bipyrimidine (**4a**) on the basis of the ^1H NMR NOE difference spectra (see the Experimental Section) and the spectral comparison with known 5-bromo-4-ethyl-2-(methylthio)-3,4-dihydropyrimidine.[4]

(1) (a) Strekowski, L. *Rocz. Chem.* **1975**, *49*, 1693. (b) Strekowski, L., *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1976**, *24*, 17. (c) Strekowski, L. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1976**, 24, 29.

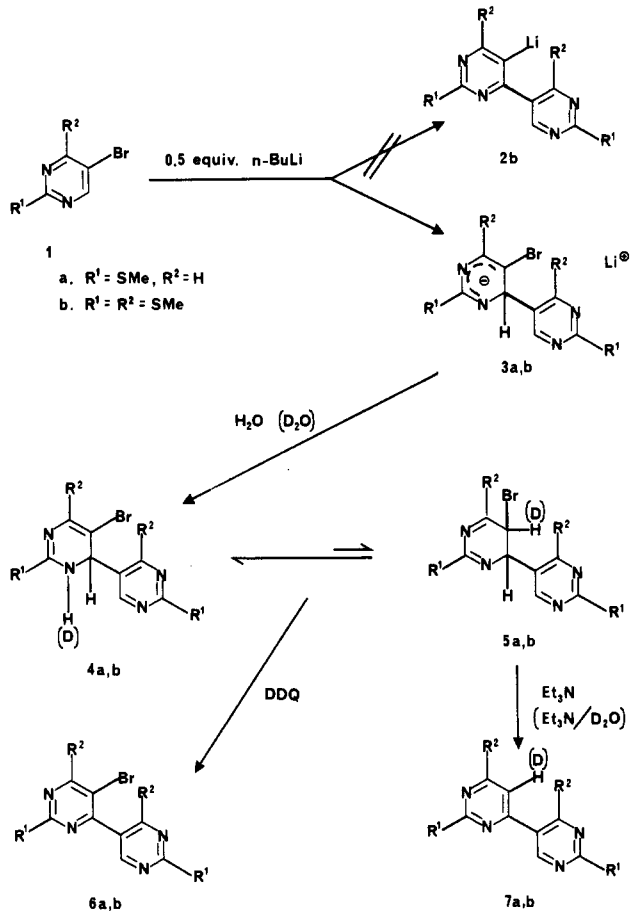
(2) Brown, D. J.; Cowden, W. B.; Strekowski, L. *Aust. J. Chem.* **1981**, *34*, 1353.

(3) Identified by comparison of its ^1H NMR spectrum with that for 2-(methylthio)pyrimidine: Albert, A.; Barlin, G. B. *J. Chem. Soc.* **1962**, 3129.

(4) Budesinsky, Z.; Vavrina, J.; Langsadl, L.; Holubek, J. *Collect. Czech. Chem. Commun.* **1980**, *45*, 539.

0022-3263/86/1951-3226$01.50/0

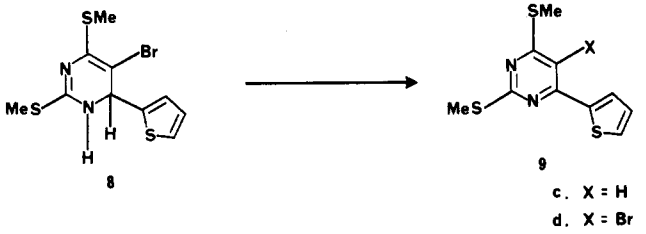
Scheme I



Compound **4a** was treated with DDQ to give 5-bromo-2,2′-bis(methylthio)-4,5′-bipyrimidine (**6a**) as the sole product. On treatment with triethylamine in benzene or sodium methoxide in methanol **4a** was dehydrobrominated to give 2,2′-bis(methylthio)-4,5′-bipyrimidine (**7a**) in a quantitative yield. The base-mediated conversion of **4a** in a MeOD solution or in benzene in the presence of D_2O gave bipyrimidine **7a** deuterated at position 5, with the deuterium excess of 92–93%.

Dihydropyrimidine **4a** is apparently produced by protonation of a σ-adduct[5] **3a** between 5-lithio-2-methylthiopyrimidine (formed from **1a** and *n*-BuLi) and **1a**. The formation of deuterated **7a** can be accounted for by a tautomeric equilibrium between **4a** and a 4,5-dihydropyrimidine **5a** and elimination of hydrogen bromide from the second tautomer.[6,7] We reasoned that the same mechanistic pathway can lead to a 4,5′-bipyrimidine **7b** in the reaction of 5-bromo-2,4-bis(methylthio)pyrimidine (**1b**) with its 5-lithio derivative, provided that **5b** is unstable and eliminates hydrogen bromide during aqueous workup. In the search for a dihydropyrimidine intermediate product the reaction mixture was neutralized with acetic acid and treated with excess DDQ at low temperature. This experiment produced 5-bromo-2,2′,4′,6-tetrakis(methylthio)-4,5′-bipyrimidine (**6b**) in a 5% yield[8] along with a 70% yield of 2,2′,4′,6-tetrakis(methylthio)-4,5′-bipyrimidine (**7b**), strongly supporting the mechanistic pathways of Scheme I.

Scheme II



It appeared that the low yield of **6b** could be due, in part, to the steric crowding of the substituents in the intermediate dihydropyrimidines. The steric hindrance would facilitate decomposition of tautomer **5b** to bipyrimidine **7b** and, at the same time, decrease interaction of the dihydropyrimidines with DDQ during aromatization. The investigation of the reaction of **1b** with 2-thienyllithium fully supported this hypothesis (Scheme II). The intermediate dihydropyrimidine **8** (or tautomer) with a relatively smaller thienyl substituent was stable in Et_2O at 0 °C and liberated hydrogen bromide at room temperature to produce 2,4-bis(methylthio)-6-(2-thienyl)pyrimidine (**9c**). This transformation could be monitored by TLC at 0 °C. Moreover, treatment of the solution of **8** with DDQ produced 5-bromo-2,4-bis(methylthio)-6-(2-thienyl)pyrimidine (**9d**) in a 61% yield.

These experiments conclusively demonstrate that the cine-substitution reaction of 4-(alkylthio)-5-bromopyrimidines with lithium reagents involves a σ-adduct, which by protonation and subsequent loss of hydrogen bromide yields a substituted pyrimidine.

Experimental Section

Melting points are uncorrected. ^1H NMR spectra were measured on a JEOL GX-270 (270 MHz) spectrometer in $CDCl_3$ with Me_4Si as internal standard. Infrared spectra were recorded on a Perkin-Elmer 257 grating infrared spectrophotometer. Mass spectra were obtained on a Varian MAT 112S instrument using an EI technique (unless otherwise stated) and operating at 70 eV. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Ga.

The reactions involving lithium reagents were conducted under a positive pressure of dry nitrogen. Ether and THF were distilled from sodium benzophenone ketyl. Analytical TLC was performed by using Merck silica gel 60 F_{254} glass-backed plates (layer thickness 0.2 mm). Preparative TLC was performed by using Analtech plates (silica gel GF, 20 cm × 20 cm × 1 mm). Flash chromatography was performed as described by Harwood.[9]

5-Bromo-2,2′-bis(methylthio)-3,4-dihydro-4,5′-bipyrimidine (4a). To a solution of 5-bromo-2-(methylthio)pyrimidine[10] (1.29 g, 6.29 mmol) in THF (30 mL) at −80 °C was added dropwise a 2.6 M solution of *n*-BuLi in hexane (1.3 mL, 3.38 mmol) over 10 min. The reaction mixture was allowed to warm up to −20 °C within 1 h and treated with water (0.5 mL) in THF (2 mL). The mixture was concentrated and extracted with $CHCl_3$ (2 × 50 mL). The extract was dried and concentrated. The crude product was chromatographed on a silica gel column by using $CHCl_3$ as eluent to give **4a** (0.75 g, 72%). An analytical sample was secured by crystallization from acetone: mp 143–145 °C; IR (Nujol) 3200, 3100, 1670 cm^{-1}; ^1H NMR δ 8.52 (s, 2 H), 6.80 (br s, 1 H, exchangeable with D_2O), 6.61 (s, 1 H), 5.32 (s, 1 H), 2.59 (s, 3 H), 2.36 (s, 3 H); MS *m/e* 330/332 (bromine isotopes, M^+), 251 (M

(5) For reviews on the addition reaction of lithium reagents to the formal 3,4-azomethine bond in pyrimidines, see: Brown, D. J. *The Pyrimidines*; Wiley-Interscience: New York, (a) 1962, (b) 1970, (c) 1985; (a) p 118, (b) Supplement 1, p 347, (c) Supplement 2, p 435.

(6) A similar mechanism has been proposed to explain cine-amination of 4-*tert*-butyl-5-halogenopyrimidines by potassium amide in liquid ammonia: Rasmussen, C. A. H.; van der Plas, H. C. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 288.

(7) Elimination of HBr and subsequent scrambling with deuteriohydropyrimidine **4a** (or tautomer) can explain the experimental fact that the deuterium excess in **7a** was not quantitative.

(8) Quenching with water or ethanol followed by treatment with DDQ did not produce **6b**.

(9) Harwood, L. M. *Aldrichimica Acta* **1985**, *18*, 25.

(10) Brown, D. J.; Foster, R. V. *Aust. J. Chem.* **1966**, *19*, 2321.

– Br). Anal. Calcd for $C_{10}H_{11}BrN_4S_2$: C, 36.26; H, 3.35; Br, 24.12. Found: C, 36.32; H, 3.39; Br, 24.19.

The ^1H NMR NOE difference spectrum was taken for a solution of **4a** in $CDCl_3$ dried with freshly activated 3A molecular sieves. Irradiation of NH (δ 6.80) resulted in a strong NOE at H-4 (δ 5.32) of the same ring and a strong NOE at H-4′ and H-6′ (δ 8.52) of the adjacent ring.

5-Bromo-2,2′-bis(methylthio)-4,5′-bipyrimidine (6a). To a solution of **4a** (0.4 g, 1.2 mmol) in toluene (20 mL) was added a solution of 2,3-dichloro-5,6-dicyanobenzoquinone (0.36 g, 1.6 mmol) in toluene (20 mL). The reaction mixture was stirred at room temperature for 3 h, then a solution of NaOH (10%, 50 mL) was added, and stirring was continued for an additional 30 min. The organic layer was separated, washed with water, dried, and evaporated to give a solid that was recrystallized from methanol: yield, 0.37 g (93%); mp 136–137 °C; ^1H NMR δ 9.00 (s, 2 H), 8.58 (s, 1 H), 2.61 (s, 3 H), 2.55 (s, 3 H); MS, *m/e* 328/330 (bromine isotopes, M^+). Anal. Calcd for $C_{10}H_9BrN_4S_2$: C, 36.48; H, 2.76; Br, 24.27. Found: C, 36.58; H, 2.79; Br, 24.19.

2,2′-Bis(methylthio)-4,5′-bipyrimidine (7a). (a) To a solution of **4a** (0.4 g, 1.2 mmol) in benzene (20 mL) was added triethylamine (3 mL). The mixture was left overnight at room temperature and then filtered from crystals of triethylamine hydrobromide. The filtrate was washed with water, dried, and evaporated to give a solid that was recrystallized from methanol: yield, 0.3 g (100%); mp 158–159 °C; ^1H NMR δ 9.11 (s, 2 H), 8.52 (d, J = 5 Hz, 1 H), 7.28 (d, J = 5 Hz, 1 H), 2.60 (s, 6 H); MS, *m/e* (relative intensity) 250 (100, M^+), 249 (6), 235 (31, $M^+ - CH_3$). Anal. Calcd for $C_{10}H_{10}N_4S_2$: C, 47.98; H, 4.03. Found: C, 47.92; H, 4.04.

(b) To a solution of sodium methoxide prepared from methanol (75 mL) and sodium (15 mg, 0.65 mmol) was added **4a** (0.2 g, 0.6 mmol). The reaction mixture was stirred for 12 h, then treated with a small piece of solid CO_2, and evaporated. The residue was extracted with benzene and worked up as described above; yield, 0.15 g (100%).

2,2′-Bis(methylthio)-4,5′-bipyrimidine-5-*d*$_1$. (a) A mixture of **4a** (0.2 g, 0.6 mmol), benzene (20 mL), and D_2O (1 mL) was stirred for 10 min and then evaporated. The residue was dissolved in benzene (20 mL) and treated with D_2O (0.5 mL) and triethylamine (3 mL). Workup as described above gave the title compound: ^1H NMR δ 7.28 (d, J = 5 Hz, 0.05 H); MS, *m/e* (relative intensity) 251 (100, M^+), 250 (14).

(b) To a solution of sodium methoxide prepared from MeOD (10 mL) and sodium (15 mg, 0.65 mmol) was added a solution of **4a** (0.2 g, 0.6 mmol) in benzene (10 mL). Workup (see above) gave deuterated **7a**: ^1H NMR δ 7.28 (0.07 H).

5-Bromo-2,2′,4′,6-tetrakis(methylthio)-4,5′-bipyrimidine (6b). To a solution of **1b** (1 g, 3.98 mmol) in THF (30 mL) at −80 °C was added dropwise a solution of *n*-BuLi in hexane (2.6 M, 0.84 mL, 2.18 mmol). The resultant mixture was kept at −45 °C for 1 h and then quenched at −45 °C with a solution of AcOH (0.13 g, 2.18 mmol) and water (0.05 mL) in THF (1 mL). A solution of DDQ (0.7 g, 3 mmol) in toluene (30 mL) was added slowly at −45 °C, and the resultant mixture was stirred and allowed to warm up to room temperature over 10 h. A solution of NaOH (10%, 50 mL) was added, and stirring was continued for an additional 30 min. The organic layer was separated, washed with water, and concentrated. Preparative TLC using CH_2Cl_2 as eluent gave 2,2′,4′,6-tetrakis(methylthio)-4,5′-bipyrimidine (**7b**, 0.47 g, 70%) identified by the ^1H NMR spectrum[1a] and 5-bromo-2,2′,4′,6-tetrakis(methylthio)-4,5′-bipyrimidine (**6b**): yield, 42 mg (5%); mp 164–165 °C; ^1H NMR δ 8.15 (s, 1 H), 2.58 (m, 12 H); MS, *m/e* 405/407 (bromine isotopes, $M^+ - CH_3$), 341 ($M^+ - Br$); CI-MS, *m/e* 421/423 (bromine isotopes, $M^+ + 1$), 327 ($M^+ + 1 - CH_3 - Br$). Anal. Calcd for $C_{12}H_{13}BrN_4S_4$: C, 34.20; H, 3.11; Br, 18.96. Found: C, 34.27; H, 3.14; Br, 18.99.

2,4-Bis(methylthio)-6-(2-thienyl)pyrimidine (9c). 2-Thienyllithium was prepared by adding *n*-BuLi in hexane (2.6 M, 4.6 mL, 12 mmol) to thiophene (1 mL, 12.5 mmol) in ether (30 mL) at 0 °C.[11] This solution was maintained at −30 °C while a solution of **1b** (3 g, 12 mmol) in ether (90 mL) was added slowly with stirring during 10 min. The reaction mixture was stirred at −20 °C for 10 min and then quenched at −20 °C with stirring with a mixture of AcOH (0.72 g, 12 mmol), water (1 mL), and THF (5 mL). After addition of toluene (125 mL) and stirring for 5 min the solution was decanted and stored below −10 °C.

Half (125 mL) of this solution was stirred with aqueous $NaHCO_3$ (10%, 50 mL) at room temperature for 30 min. The organic layer was separated and evaporated to give crude **9c**, which was purified by flash chromatography using a mixture of CH_2Cl_2 and hexanes (1:1) as eluent and recrystallized from ethanol: yield, 1.37 g (90%); mp 101–101.5 °C; ^1H NMR δ 7.69 (2 d, J_1 = 1.2 Hz, J_2 = 3.8 Hz, 1 H), 7.47 (2 d, J_1 = 1.2 Hz, J_3 = 5.0 Hz, 1 H), 7.11 (2 d, J_2 = 3.8 Hz, J_3 = 5.0 Hz, 1 H), 7.08 (s, 1 H), 2.62 (s, 3 H), 2.60 (s, 3 H); MS *m/e* 254 (M^+), 293 ($M^+ - CH_3$). Anal. Calcd for $C_{10}H_{10}N_2S_3$: C, 47.21; H, 3.96. Found: C, 47.16; H, 3.97.

5-Bromo-2,4-bis(methylthio)-6-(2-thienyl)pyrimidine (9d). A solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (2.27 g, 10 mmol) in the THF (20 mL) was added at −10 °C to the remaining solution (125 mL) from the experiment above. The mixture was stirred at −10 °C for 10 h and then was allowed to reach room temperature within 5 h. A solution of NaOH (10%, 50 mL) was added, and stirring was continued for an additional 30 min. The organic layer was separated, washed with water, dried, and evaporated to give a mixture of **9c** and **9d** (1:3), which was separated by flash chromatography using a mixture of CH_2Cl_2 and hexanes (1:1) as an eluent. Final recrystallization from hexanes gave 1.2 g (61%) of **9d**: mp 119–120 °C; ^1H NMR δ 8.27 (2 d, J_1 = 1.2 Hz, J_2 = 3.8 Hz, 1 H), 7.51 (2 d, J_1 = 1.2 Hz, J_3 = 5.0 Hz, 1 H), 7.12 (2 d, J_2 = 3.8 Hz, J_3 = 5.0 Hz), 2.58 (s, 3 H), 2.53 (s, 3 H); MS, *m/e* 332/334 (bromine isotopes, M^+), 253 ($M^+ - Br$). Anal. Calcd for $C_{10}H_9BrN_2S_3$: C, 36.04; H, 2.72; Br, 23.98. Found: C, 35.97; H, 2.75; Br, 23.94.

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Registry No. **1a**, 14001-67-3; **1a** (5–Li), 103191-83-9; **1b**, 60186-81-4; **3b**, 103191-82-8; **4a**, 103191-85-1; **5b**, 103191-84-0; **6a**, 103191-86-2; **6b**, 103191-89-5; **7a**, 103191-87-3; **7a** (5-*d*), 103191-88-4; **7b**, 60186-83-6; **9c**, 103191-90-8; **9d**, 103191-91-9; 2-thienyllithium, 2786-07-4; thiophene, 110-02-1.

(11) Brown, D. J.; Cowden, W. B.; Strekowski, L. *Aust. J. Chem.* **1982**, *35*, 1209.

A Convenient Procedure for the Preparation of 4(5)-Cyanoimidazoles

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During a recent synthetic program we required 4(5)-cyanoimidazoles **3** and 4(5)-cyano-2,2′-bi-1*H*-imidazoles (**3**, R = 2-imidazolyl).[1] It was surprising to us to find no general and/or facile method for the preparation of these compounds.[2-4] In this note we wish to report a facile, high yield method for the preparation of 4(5)-cyanoimidazoles **3** and the corresponding biimidazoles.

The conversion of 2-(trifluoromethyl)imidazoles to 2-cyanoimidazoles has been reported.[6,7] However, the

(1) These compounds proved to be of biological interest: Matthews, D. P.; Whitten, J. P.; McCarthy, J. R.; Marshall, F.; Wenger, M. A.; Burkhard, T., manuscript in preparation.

(2) 4(5)-Cyano-2,2′-bi-1*H*-imidazoles are unreported in the literature. For two methods to **3a**, see ref 3 and 4.

(3) Mitsuhashi, K.; Itho, E.; Kawahara, T.; Tanaka, K. *J. Heterocycl. Chem.* **1983**, *20*, 1103.

(4) Ferris, J. P.; Trimmer, R. W. *J. Org. Chem.* **1976**, *41*, 19.

(5) For a convenient preparation of 2,2′-1*H*-biimidazole, see: Matthews, D. P.; Whitten, J. P.; McCarthy, J. R. *Synthesis* **1986**, 336.

0022-3263/86/1951-3228$01.50/0