hyde (8.0 g; 0.066 mol), and sodium methoxide (6.32 g; 0.117 mol) in 300 ml of methanol was heated under reflux for 12 hr. After cooling, 11.96 g (0.12 mol) of concentrated H_2SO_4 was cautiously added. The resultant solution was heated under reflux for 24 hr. After neutralization with aqueous sodium bicarbonate, the mixture was extracted with chloroform. After removal of the volatiles at the water pump, the residue was distilled at 0.01 mm. A fraction of bp 138–140° consisting of 11.54 g (87%) was obtained: λ_{max} (CCl_4) 5.79 μ; δ (CCl_4) 2.35 (s, 3), 3.78 (s, 3), 7–8 (m, 5).

Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51; N, 6.69. Found: C, 71.40; H, 5.63; N, 6.86.

Preparation of 3-Oxo-1*H*-pyrrolo[3,4-*b*]quinoline (1). A solution of **2** (19.51 g; 0.097 mol) in 50 ml of carbon tetrachloride was added, with stirring, to a solution of *N*-bromosuccinimide (17.05 g; 0.096 mol) and dibenzoyl peroxide (1.09 g; 0.0045 mol) in 200 ml of the same solvent. The temperature was raised over 1 hr to the boiling point and heating under reflux was continued for an additional 18 hr. After removal of the succinimide (lighter than the solvent) by filtration, the volatiles were evaporated at the water pump. The residual bromomethyl compound, **3**, was dissolved in 500 ml of methanol. Gaseous ammonia was continuously bubbled through the solution as concentrated ammonium hydroxide (9 drops) was added. Heating under reflux was continued for 2.5 hr. A white solid separated and was collected by filtration. Additional solid was obtained by concentration of the methanolic solution. Recrystallization of the combined solids from 95% ethanol yielded 15.28 g (86%) of compound **1**: mp 295–302° dec (lit.[6] 280–283° dec; λ_{max} (nujol) 3.05, 5.91μ; δ (CF_3CO_2H) 5.17 (s, 2), 8.3–9.2 (m, 4), 9.96 (s, 1), 10.04 (s, 1).

Anal. Calcd for $C_{11}H_8N_2O$: C, 71.73; H, 4.38; N, 15.21. Found: C, 71.49; H, 4.39; N, 14.99.

Conversion of Methyl *o*-Toluate to Phthalimidine (5). A mixture prepared by adding *N*-bromosuccinimide (114 g; 0.64 mol) and dibenzoyl peroxide (1.29 g; 5 mmol) to a solution of methyl *o*-toluate (90 g; 0.66 mol) in 350 ml of carbon tetrachloride was heated under reflux for 4 hr. After cooling and filtration of the succinimide, the solvent was evaporated at the water pump. The residue (125 g) consisting of **4** was dissolved in 500 ml of methanol. To this was added 150 ml of concentrated ammonia and the system was brought to reflux. Anhydrous ammonia was bubbled through. After cooling, the volatiles were removed at the water pump. The solid residue was washed with water and then with ether. The phthalimidine (48 g, 60%) upon recrystallization from water had a melting point of 155–156° (lit.[14] 150–151°).

Condensation of Phthalimidine (5) with Diethyl Acetone-1,3-dicarboxylate (6). (i) At Atmospheric Pressure (Formation of 8). Compound **5** (500 mg; 4.2 mmol) was added to excess (6 ml) **6**. The system was heated at 160–165° for 2 hr. On cooling, white crystals separated and were collected. More product was recovered by chromatography of the mother liquor on 300 g of silica gel by elution with 1:1 ether–petroleum ether. The elution order was **6** > **8** > **5**. The combined solid, **8**, mp 138–139°, weighed 923 mg (77% conversion; 93% yield). In addition compound **5** (100 mg; 20%) was recovered: *m/e* 317 (parent); λ_{max} ($CHCl_3$) 5.80, 5.89 (sh), 6.18 (sh), 6.20 μ; δ ($CDCl_3$) 1.25 (t, J = 7 Hz, 6 H, overlapping triplets), 4.20, 4.22 (2 q, J = 7 Hz for each, 4 H), 4.68 + 4.70 (2 s, 4 H), 5.65 (s, 1 H), 7.2–8.0 (m, 4 H).

Anal. Calcd for $C_{17}H_{19}NO_5$: C, 64.35; H, 5.99; N, 4.44. Found: C, 64.36; H, 6.07; N, 4.40.

(ii) **At Reduced Pressure (Formation of 8 + 9).** Phthalimidine (**5**) (1.0 g; 7.55 mmol) was added to an excess 12 ml of **6**. The system was connected to an aspirator (15–20 mm). It was heated at 160–165° for 30 min. After cooling the total mixture was chromatographed on *ca.* 600 g of silica gel. Elution with 1:1 ether–petroleum ether first removed **6**. After this, 0.56 g (23%) of **8** was obtained. The final product eluted was compound **9**: 1.28 g (59% yield); mp 94–95°; *m/e* 289 (parent); λ_{max} ($CHCl_3$) 5.80 (sh) 5.85, 5.92 (sh), 6.20 μ; δ ($CDCl_3$)[15] 1.30 (t, J = 7 Hz, 3 H), 3.72 (s, 2 H), 4.05–4.40 (q, J = 7 Hz, + s δ = 4.3, total = 4 H), 4.83 (s, 2 H), 7.3–8.0 (m, 4 H).

Anal. Calcd for $C_{15}H_{15}NO_5$: C, 62.28; H, 5.19; N, 4.84. Found: C, 62.57; H, 5.15; N, 4.75.

Reaction of 5 with Methyl Acetoacetate. Formation of 10. Phthalimidine (500 mg; 3.7 mmol) and methyl acetoacetate (1 g; 8.5 mmol) were heated in a sealed tube at 200° for 18 hr. After cooling, the contents were dissolved in chloroform. Addition of petroleum ether gave a precipitate which was recrystallized from ethanol to give **10**: 410 mg; 46% yield; mp 120–122°; *m/e* 231 (parent); λ_{max} 5.80, 5.85, 6.20 μ; δ ($CDCl_3$) 2.76 (s, 3 H), 3.70 (s, 3 H), 4.55 (s, 2 H), 5.95 (s, 1 H), 7.2–8.0 (m, 4 H).

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Registry No.—**1**, 34535-42-7; **2**, 53821-46-8; **5**, 480-91-1; **6**, 105-50-0; **8**, 53821-47-9; **9**, 53821-48-0; **10**, 53821-49-1; 2-oxobutyric acid, 600-18-0; *o*-aminobenzaldehyde, 529-23-7; *N*-bromosuccinimide, 128-08-5; methyl *o*-toluate, 89-71-4; methyl acetoacetate, 105-45-3.

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(10) Although starting **1** was recovered in high yield (starting with 368 mg, 320 were recovered) the mass spectrum of the mother liquors exhibits a small peak at *m/e* 368 which corresponds to **1** + **6** − H_2O, *i.e.*, the enamide analog of **7**. Thus, there may be a slight amount of enamine formation even here.
(11) We thank Dr. Sugasawa for making the details of his excellent procedure available to us prior to publication.
(12) The double bond geometry is unspecified.
(13) Melting points are uncorrected. Nmr spectra were measured at 60 MHz on Varian Associates A60, A60D, and T60 spectrometers with tetramethylsilane as internal standard. Data are reported in parts per million (δ) from TMS. Infrared spectra were obtained from Perkin-Elmer 137 or 247 spectrophotometers. Mass spectra were measured on an LKB 9 combined glc–mass spectrometer by direct insertion. Analyses were conducted by Galbraith Inc., Knoxville, Tenn.
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Synthesis of Benziodathiazoles

Howard Jaffe and J. E. Leffler*

Florida State University, Tallahassee, Florida 32306

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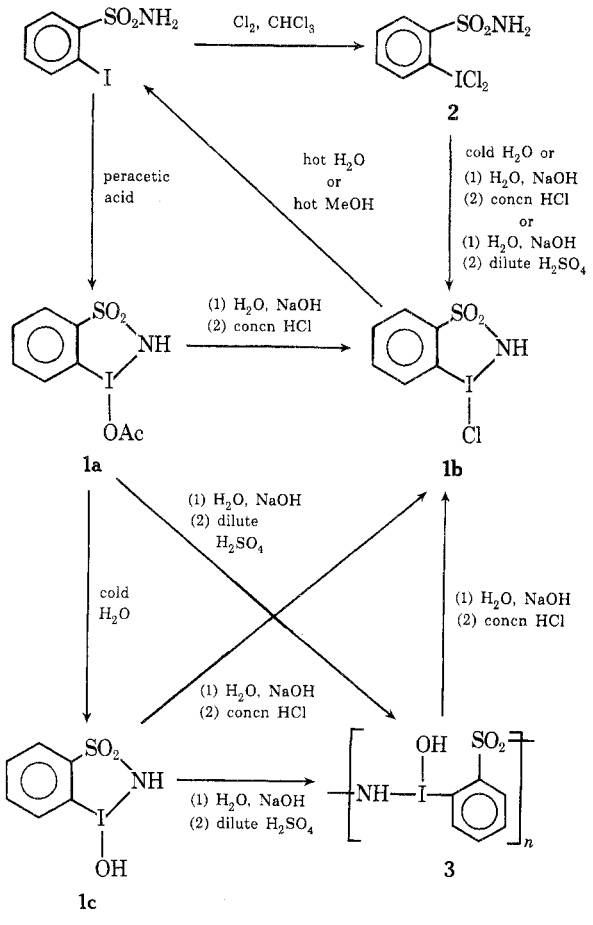
A number of heterocyclic compounds whose rings contain polyvalent iodine have been described. Recently we have reported on the synthesis and properties of *o*-iodosophenylphosphoric acid and its methyl ester to which we have assigned the six-membered cyclic structures 1,3-dihydroxy-1*H*-1,2,4,3-benziodadioxaphosphorin 3-oxide and 1-methoxy-3-hydroxy-1*H*-1,2,4,3-benziodadioxyphosphorin-3-oxide.[2]

The present note describes the synthesis of polyvalent iodine derivatives of *o*-iodobenzenesulfonamide to which we have assigned the five-membered benziodathiazole structures **1a–c**. Entry into the benziodathiazole system is achieved *via* 1-acetoxy-1,2-dihydro-1,3,2-benziodathiazole 3,3-dioxide (**1a**) (Scheme I) synthesized by peracetic acid oxidation of *o*-iodobenzenesulfonamide or *via* 1-chloro-1,2-dihydro-1,3,2-benziodathiazole 3,3-dioxide (**1b**) synthesized by hydrolysis of *o*-(dichlorido)iodosobenzenesulfonamide (**2**). The latter is synthesized by chlorination of *o*-iodobenzensulfonamide. Compound **1b** is also obtained by acidification of a NaOH solution of **1a** or **2** (Scheme I).

Scheme I



Hydrolysis of **1a** gives 1-hydroxy-1,2-dihydro-1,3,2-benziodathiazole 3,3-dioxide (**1c**). Acidification of a NaOH solution of **1a** or **1c** with sulfuric acid gives an insoluble white powder (**3**) which is probably a polymeric form of **1c**.

Benziodathiazoles **1a–c** and the polymer **3** are interconvertable as shown in Scheme I. In addition both **1b** and **3** can be regenerated from their NaOH solutions by acidification (Scheme I).

Treatment of **1b** with boiling methanol or water results in the reduction of its polyvalent iodine function to give *o*-iodobenzenesulfonamide.

Structures were assigned mainly on the basis of ir and pmr spectra rather than elementary analyses. The latter suffer from poor reproducibility of the analyses of NSI or NSICl compounds as well as the instability of some of the compounds.

Spectroscopic Properties of 1b. The ir spectrum of **1b** has S=O stretch bands at 1345 and 1160 cm^{-1} and sharp N–H stretch peaks at 3352 and 3249 cm^{-1}.

The nmr spectrum in DMSO-d_6 has a broad D_2O-exchangeable signal for the NH proton. The two protons ortho to sulfur and iodine appear downfield from the other aromatic protons as a multiplet approximating two triplets at τ 1.87 and 1.99, respectively. The position of the signal from the proton ortho to I is consistent with a covalent structure rather than an ionic one such as $>I^+Cl^-$. For example, the proton ortho to positively charged iodine in 3-butyl-2-phenylbenziodolium chloride[4] gives a signal much further downfield at τ 1.05.

Spectroscopic Properties of 1a. The broad bands at 3199 and 3134 cm^{-1} and the band in the low carbonyl region (1624 cm^{-1}) in the infrared spectrum of **1a** would be consistent with either the >I–O acetyl and N–H structure shown or an N acetyl and >I–OH structure.[5-7]

However, the nmr spectrum of **1a** in DMSO-d_6 displays a methyl singlet at τ 8.09 and aromatic absorption at τ 2.90–1.39. Underlying the latter is a D_2O-exchangeable absorption attributed to the NH group occurring in the same region observed for this and similar groups in the spectra of **1b, 1c, 3,** and *o*-iodobenzenesulfonamide. The absence of any upfield OH absorption as in the spectra of **1c** and **3** excludes the 2-acetyl structure.

Spectroscopic Properties of 1c and 3. The ir spectrum of 1-hydroxy-1,2-dihydro-1,3,2-benziodathiazole 3,3-dioxide (**1c**) displays a single NH band at 3266 cm^{-1} and broad OH absorption with maxima at 3154 and 3082 cm^{-1}.

Compound **3** has broad bands in the ir corresponding for the most part to an envelope of the ir bands of **1c.** The nmr spectrum of **3** is essentially identical to that of **1c** except for a downfield shift of the OH peak. Analytical data suggest an empirical formula $C_6H_6INO_3S$.

Experimental Section

Sodium *o*-iodobenzenesulfonate hydrate was made from diazotized orthanilic acid and KI by the general procedure of Vogel.[8] The product appeared on the basis of nmr to contain about 1.4 mol of water. It was converted to the acid chloride by reaction with $POCl_3$, and then into the amide.[9]

***o*-(Dichlorido)iodosobenzenesulfonamide (2).** A stirred solution of 0.75 (.0026 mol) of *o*-iodobenzenesulfonamide in 200 ml of dry $CHCl_3$ was chilled in an ice bath and treated with dry chlorine for 1 hr. The yellow precipitate that had formed after several minutes was filtered, washed with carbon tetrachloride, and dried to give 0.88 g (98%) of *o*-(dichlorido)iodosobenzenesulfonamide (**2**) as a yellow powder. Storage in the freezer prevented decomposition. Analysis of **2** was not attempted, but its color and solubility are typical of iodosodichlorides.

1-Acetoxy-1,2-dihydro-1,3,2-benziodathiazole 3,3-Dioxide (1a). A suspension of 12.0 g (.0424 mol) of *o*-iodobenzenesulfonamide in 28 ml of 40% peracetic acid was vigorously stirred until after *ca.* 4 hr a clear yellow solution resulted. Stirring was continued for an additional 21 hr during which a thick white suspension gradually formed. Filtration and thorough drying at high vacuum gave 11.5 g (80%) of 1-acetoxy-1,2-dihydro-1,3,2-benziodathiazole 3,3-dioxide (**1a**) as a white solid: mp 146–147° dec to red oil with gas evolution (tube in at 145°, heated at 1–2°/min); ir (Nujol and Fluorolube) 3199 (NH), 3134 (NH), 3086, 3057, 2985 (CH_3), 2934 (CH_3), 1624 (C=O), 1593, 1560, 1436, 1371, 1359, 1320 (S=O), 1309 (S=O), 1294, 1218, 1169 (S=O), 1159 (S=O), 1127, 1099, 1007, 930, 869, 799, 773, 766, 735, 709, 696, 674, 663, and 647 cm^{-1}; nmr (DMSO-d_6) τ 1.83–2.52 (m, 5, aromatic H and NH [D_2O exchangeable]) and 8.09 (s, 3, OAc).

Anal.[10] Calcd for $C_8H_8INO_4S$: C, 28.17; H, 2.36; S, 9.40; equivalent wt, 170.5. Found: C, 26.83; H, 1.90; S, 10.01; equivalent wt, 166.4 (iodometric).

1-Chloro-1,2-dihydro-1,3,2-benziodathiazole 3,3-Dioxide (1b). To a vigorously stirred fresh solution of 2.00 g (0.00587 mol) of 1-acetoxy-1,2-dihydro-1,3,2-benziodathiazole 3,3-dioxide (**1a**) in 20 ml of 1 *N* NaOH was added dropwise an excess of concentrated HCl. The resulting yellow precipitate was filtered, air dried on the filter, and pumped at high vacuum to give 1.79 g (96%) of 1-chloro-1,2-dihydro-1,3,2-benziodathiazole 3,3-dioxide (**1b**) as a yellow solid: mp 105–106° dec with gas evolution (tube in at 105° and heated at 1–2°/min); ir (Nujol and Fluorolube) 3352 (NH), 3249 (NH), 3084, 3072, 1568, 1560, 1442, 1429, 1345 (S=O), 1336 (S=O), 1278, 1260, 1183, 1160 (S=O), 1133, 1120, 1103, 1043, 1032, 1019, 989, 914, 819, 773, 764, 735, 703, 694, 682, and 647 cm^{-1}; nmr (DMSO-d_6) τ 1.78–2.08 (m approximating two triplets centered at 1.87 and 1.99, 2, protons ortho to iodine and sulfur), 2.26–2.97 (m, 2, other aromatic H), *ca.* 1.03–2.67 (broad, 1, NH, exchangeable with D_2O).

Anal. Calcd for $C_6H_5ClINO_2S$: C, 22.69; H, 1.59; S, 10.10; equivalent wt, 158.7. Found: C, 23.01; H, 1.35; S, 10.20; equivalent wt, 162.1 (iodometric).

This compound with identical ir spectrum was also obtained in 80% yield by hydrolysis of **2** in water or in NaOH followed by neutralization with either H_2O or H_2SO_4.

1-Hydroxy-1,2-dihydro-1,3,2-benziodathiazole 3,3-Dioxide (1c). A suspension of 2.00 g (.00587 mol) of 1-acetoxy-1,2-dihydro-1,3,2-benziodathiazole 3,3-dioxide (**1a**) in 40 ml of water was vigorously stirred for 16 hr. Filtration, washing sparingly with water,

and thorough drying at high vacuum gave 1.69 g (96%) of 1-hydroxy-1,2-dihydro-1,3,2-benziodathiazole 3,3-dioxide as a white solid: mp 146° explodes (tube in at 145° and heated at 1–2°/min); ir (Nujol and Fluorolube) 3266 (NH), 3134 (OH), 3082 (OH), 1556, 1439, 1319, 1309 (S=O), 1241, 1181, 1167 (S=O), 1159 (S=O), 1140, 1126, 1112, 1099, 1083, 1116, 1006, 934, 898, 852, 784, 770, 750, 734, 700, 669, and 645 cm^{-1}; nmr (DMSO-d_6) τ 1.82–2.56 (m, 5, aromatic H and HN [D_2O exchangeable]) and 6.68 (broad, 1, OH, D_2O exchangeable).

Anal.[10] Calcd for $C_6H_6INO_3S$: C, 24.09; H, 2.02; S, 10.72; equivalent wt, 149.5. Found: C, 25.21; H, 1.79; S, 10.71; equivalent wt, 145.9 (iodometric).

Compound 3. Method A. To a vigorously stirred solution of 0.50 g (0.0015 mol) of 1-acetoxy-1,2-dihydro-1,3,2-benziodathiazole 3,3-dioxide (**1a**) in 2.5 ml of 1 *N* NaOH was added excess dilute H_2SO_4 dropwise. The resulting precipitate was filtered, washed with cold water, and dried in high vacuum to give 0.38 g (87%) of a pale yellow solid (**3**): mp 147° explodes (tube in at 145° and heated at 1–2°/min); ir (Nujol and Fluorolube) 3504 (br), 3104 (br), 3080 (br), 1630 (br), 1555, 1435, 1293 (br), 1153, 1124, 1094, 1031, 1009, 893 (br), 766, 735, and 703 cm^{-1}, nmr (DMSO-d_6) τ 1.83–2.56 (m, 5, aromatic H and NH [D_2O exchangeable]) and 4.69 (br, 1, OH, D_2O exchangeable).

Anal.[10] Calcd for $C_6H_6INO_3S$: C, 24.09; H, 2.02; S, 10.72; equivalent wt, 149.5. Found: C, 24.63; H, 1.57; S, 11.77; equivalent wt, 151.8 (iodometric).

Method B. To a vigorously stirred solution of 0.50 g (0.0017 mol) of 1-hydroxy-1,2-dihydro-1,3,2-benziodathiazole 3,3-dioxide (**1c**) in 5 ml of 1 *N* NaOH was added dropwise excess dilute H_2SO_4. The resulting precipitate was filtered, washed with cold water, and dried under high vacuum to give 0.33 g (66%) of **3** with identical ir.

Conversion of 1c to 1b. To a vigorously stirred solution of 0.50 g (0.0017 mol) of **1c** in 10 ml of 1 *N* NaOH was added dropwise concentrated HCl. The resulting precipitate was filtered, washed with cold water, and dried under vacuum to give 0.50 g (94%) of **1b**.

Conversion of 3 to 1b. To a vigorously stirred solution of 0.50 g (0.0017 mol) of **3** in 3.0 ml of 1 *N* NaOH was added excess concentrated HCl, dropwise. The resulting precipitate was filtered, washed with cold water, and dried under vacuum to give 0.43 g (81%) of **1b**.

Regeneration of 1b. To a vigorously stirred solution of 0.25 g (0.00079 mol) of **1b** in 5.0 ml of 1 *N* NaOH was added dropwise excess concentrated HCl. The resulting gummy precipitate was triturated in the mother liquor to give a granular precipitate. Filtration, washing sparingly with cold water, and drying under vacuum gave 0.20 g (80%) of **1b** with unchanged ir.

Regeneration of 3. To a vigorously stirred solution of 0.20 g (0.00067 mol) of **3** in 2.0 ml of 1 *N* NaOH was added dropwise excess dilute H_2SO_4. The resulting precipitate was filtered, washed with cold water, and dried under vacuum to give 0.08 g (40%) of **3** with unchanged ir.

Reduction of 1b in Refluxing Methanol. A suspension of 0.30 g (0.00095 mol) of **1b** in 2.0 ml of anhydrous methanol was refluxed for 5 min to give a yellow solution with a sharp odor. Upon cooling 0.10 g (37%) of *o*-iodobenzenesulfonamide was deposited.

Reduction of 1b in Hot Water. A suspension of 0.50 g (0.00150 mol) of **1b** in 15 ml of water was boiled for 10 min to give a pale yellow solution with a sharp odor. Upon cooling 0.20 g (46%) *o*-iodobenzenesulfonamide (identified by ir) was deposited.

Registry No.—**1a**, 53730-93-1; **1a** polymer, 53730-94-2; **1b**, 53730-97-5; **1c**, 53730-95-3; **1c** polymer, 53730-96-4; **2**, 53730-98-6; **3**, 53730-92-0; *o*-iodobenzenesulfonamide, 53730-99-7.

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Synthesis of 3,4,5-Tris(aryl- and alkylthio)-2,6-pyridinedicarbonitriles

Christian T. Goralski* and Thomas E. Evans[1]

Halogens Research Laboratory, The Dow Chemical Company, Midland, Michigan 48640

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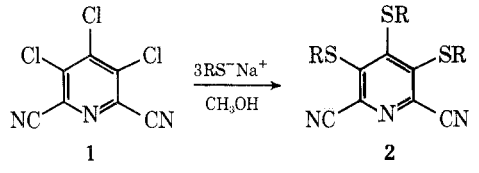
Although aromatic, nucleophilic displacements are well known for pentachloropyridine[2] and related halogenated pyridines, multiple displacements are often difficult and slow. In this note we describe the reaction of 3,4,5-trichloro-2,6-pyridinedicarbonitrile (**1**),[3] in which all three chlorines are activated toward nucleophilic aromatic substitution, with 3 equiv of a sodium thiolate in methanol at room temperature to afford the corresponding 3,4,5-tris(aryl- or alkylthio)-2,6-pyridinedicarbonitrile (**2**, eq 1, Table I). The reaction is extremely rapid, beginning as soon as



1 2 (1)

the reactants are mixed. It appears that once one thio group is introduced, the remaining two chlorines are very rapidly replaced as evidenced by the isolation of 3,4,5-tris(methylthio)-2,6-pyridinedicarbonitrile (**2**, R = CH_3) from the reaction of **1** with 1 equiv of sodium methanethiolate.

Table I
3,4,5-Tris(aryl- and alkylthio)-2,6-pyridinedicarbonitriles (2)

R	Mp, °C	Yield, %	Registry no.
CH_3	98–100	90	35646-45-8
C_6H_5	125–127	94	53862-54-7
4-$CH_3C_6H_4$	189–190	91	53862-55-8
4-$(CH_3)_3CC_6H_4$	150–152	48	53862-56-9
4-BrC_6H_4	158–160	92	53862-57-0
2-$C_{10}H_7$	165–167	67	53862-58-1

The structure of **2**, R = CH_3, and hence that of the entire series, was confirmed by its carbon-13 NMR spectrum (Table II), which is clearly indicative of the symmetrical nature of the molecule. The 100-MHz proton spectrum of **2**, R = CH_3 displays singlets at δ 2.62 and 2.70, in a ratio of 1:2, which further confirms the symmetry of the molecule and substantiates the presence of methylthio groups in different environments in a ratio of 1:2.

Table II
^{13}C NMR of 2, R = CH_3

	Chemical shift, δ [a]
C_2 and C_6	156.9
C_4	146.0
C_3 and C_5	134.4
C≡N	114.8
CH_3S	19.3

[a] Recorded in parts per million downfield from tetramethylsilane.

Experimental Section[4]

3,4,5-Tris(aryl- and alkylthio)-2,6-pyridinedicarbonitriles. In a 500-ml, single-neck flask equipped with a magnetic stirrer and