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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(3) B. Altenkirk and S. S. Israelstam, *J. Org. Chem.*, **27**, 4532 (1962).
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Synthesis of 3,4,5-Tris(aryl- and alkylthio)-2,6-pyridinedicarbonitriles

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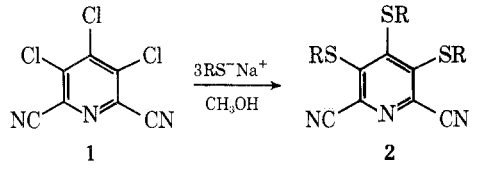
Although aromatic, nucleophilic displacements are well known for pentachloropyridine[2] and related halogenated pyridines, multiple displacements are often difficult and slow. In this note we describe the reaction of 3,4,5-trichloro-2,6-pyridinedicarbonitrile (**1**),[3] in which all three chlorines 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

a reflux condenser fitted with a calcium chloride drying tube were placed 300 ml of methanol and 2.76 g (0.12 g-atom) of sodium metal. After all of the sodium had reacted, 0.12 mol of thiol was added and the resulting solution was stirred for 15 min. To the thiolate solution, 9.28 g (0.04 mol) of 3,4,5-trichloro-2,6-pyridinedicarbonitrile was added. The solution immediately became yellow in color, and a slight exotherm was observed. After stirring for several minutes, the contents of the flask solidified to a bright yellow, solid mass. The solid was filtered off and vacuum dried. The solid was recrystallized from methylene chloride–hexane or ethanol when necessary.

Reaction of 1 with 1 Equiv of Sodium Methanethiolate. In a 1-l., three-neck flask equipped with a magnetic stirrer, a rubber septum, and a reflux condenser fitted with a calcium chloride drying tube were placed 600 ml of methanol and 2.30 g (0.10 g-atom) of sodium metal. After all of the sodium had reacted, 6 ml of methanethiol (*stench*) was added to the methanol solution. The solution was allowed to stir for 0.5 hr, and then 23.25 g (0.10 mol) of 3,4,5-trichloro-2,6-pyridinedicarbonitrile was added. The reaction mixture immediately became yellow in color. The reaction mixture was heated to reflux (to make the system homogeneous) and then allowed to cool slowly to room temperature. Flat, white crystals separated which were filtered and dried to give 9.50 g of recovered 3,4,5-trichloro-2,6-pyridinedicarbonitrile, mp 198–200°. The methanol was removed from the filtrate in vacuo, leaving, after vacuum drying, 12.77 g of a pale yellow solid. The solid was treated with 100 ml of boiling 95% ethanol, and the resulting yellow solution was filtered. Upon cooling, long, bright yellow needles separated. The crystallization liquor was decanted, and the remaining needles were recrystallized from 50 ml of 95% ethanol to give, after vacuum drying, 0.78 g of 3,4,5-tris(methylthio)-2,6-pyridinedicarbonitrile (**2**, R = CH_3), mp 98–100°. Cooling the previously decanted crystallization liquor (see above) gave an additional 0.33 g, mp 98–100°.

Registry No.—**1**, 17824-85-0; sodium methanethiolate, 5188-07-8; sodium benzenethiolate, 930-69-8; sodium 4-methylbenzenethiolate, 10486-08-5; sodium 4-*tert*-butylbenzenethiolate, 5787-50-8; sodium 4-bromobenzenethiolate, 13457-82-4; sodium 2-naphthalenethiolate, 875-83-2.

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(1) Analytical Laboratory, The Dow Chemical Co.

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(3) This compound is prepared by the vapor phase chlorination of 2,6-pyridinedicarbonitrile. See W. H. Taplin III (to the Dow Chemical Co.), U.S. Patent 3,420,833 (Jan 7, 1969); R. M. Bimber (to Diamond Shamrock Corp.), U.S. Patent 3,325,503 (June 13, 1967).

(4) All melting points are uncorrected. All new compounds gave satisfactory elemental analyses and ir and NMR spectra. The 100-MHz proton spectra were recorded on a Varian HA-100 spectrometer with an internal lock on tetramethylsilane. The carbon-13 spectrum was recorded at 25.2 MHz on a Varian XL-100-15 spectrometer equipped with a Digilab NMR-3 Fourier transform system.

A Convenient Preparation of Unsymmetrically Substituted Pyrroles, Furans, and Thiophenes

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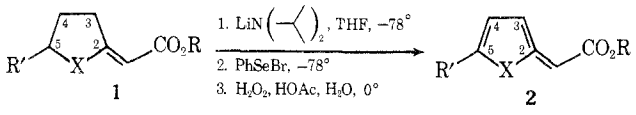
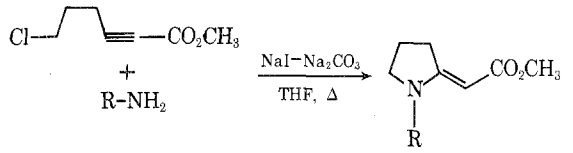
We wish to report a facile and versatile synthesis of substituted pyrroles, furans, and thiophenes. During one phase of a study of conjugated enamines,[1] we have found that enamino esters (**1a** and **1b**), enol ether esters (**1c**), or thioenol ether esters (**1d**) undergo γ-alkylation with benzeneselenenyl bromide. Oxidation (H_2O_2) and elimination of benzeneseleninic acid, followed by in situ double bond isomerization, afforded pyrrole (**2a** or **2b**), furan (**2c**), or thiophene (**2d**) in good yield.



	% yield
a, X = N—$(CH_2)_7$—$C_6H_3(OCH_3)_2$; R = CH_3; R′ = H	**2a**, 86
b, X = N—$(CH_2)_5CO_2CH_3$; R = CH_3; R′ = H	**2b**, 71
c, X = O; R = CH_2CH_3; R′ = CH_3	**2c**, 94
d, X = S; R = CH_2CH_3; R′ = CH_3	**2d**, 95

Spectral analyses of the products were consistent with the proposed structures.[2] The most notable change in going from **1** to **2** was the disappearance of vinyl absorptions in the ^1H NMR spectra of **1** and appearance of low-field methylene singlets in **2**. Also, disappearance of aliphatic ring proton absorptions of **1** and appearances of low-field multiplets characteristic of pyrroles, furans, and thiophenes were consistent with the assigned product. The infrared and ultraviolet spectra also showed absorption changes characteristic of conjugated esters being converted to unconjugated esters.[3]

The utility of this facile conversion is further supported by the ease of preparation of the enamino esters. For example, **1b** was prepared by concomitant Michael addition–alkylation of methyl 6-aminohexanoate with methyl 6-chloro-2-hexynoate in the presence of sodium iodide and sodium carbonate. Overnight reflux under nitrogen in THF



typically gave an 85% yield of enamino ester on work-up. Benzylamine, butylamine, phenethylamines, and ammonia have also been used in this process (70–95%).

Similarly, the relative simplicity of the preparation of **1c** and **1d** by epoxide or sulfide ring opening with the dianion of ethyl acetoacetate allows for the synthesis of a variety of tetrahydrofurylidene acetates and tetrahydrothiophenylidene acetates, and consequently a variety of furans and thiophenes, respectively.[4] The γ-alkylation of enamino esters[1] coupled with this aromatization sequence should give 3-substituted pyrroles.[5]

It is interesting to note that in this work we have not found evidence for sulfur oxidation in the oxidation–elimination sequence. This seems to confirm other qualitative reports of the relative ease of selenium oxidation compared to that of sulfur.[6]

Experimental Section[7]

Methyl *N*-(5-Carbomethoxypentyl)-α-pyrrolidinylideneacetate (1b). Methyl 6-chloro-2-hexynoate (3.13 g), methyl 6-aminohexanoate (3.00 g), sodium iodide (3.75 g), and sodium carbonate (2.65 g) were added to tetrahydrofuran (anhydrous, 60 ml) and refluxed for 20 hr under an atmosphere of nitrogen. After cooling, the reaction mixture was poured into water (100 ml) and methylene chloride (100 ml). The organic layer was separated, and the aqueous layer was extracted with methylene chloride (3 × 50 ml). The combined organic extracts were washed with aqueous sodium chloride (saturated, 50 ml), dried (Na_2SO_4), and concentrated under reduced pressure to give 5.55 g of crude product. Chromatography on alumina (50 g, Woelm activity grade III) with chloroform gave 5.25 g (100%) of **1b**: λ_{max} (film) 2950, 2860, 1735 (s), 1680 (s), 1595 (vs), 1435, 1140 (vs), 1060, and 780 cm^{-1}; δ_{TMS} ($CDCl_3$) 4.50 (t, J = 1.5 Hz, vinyl), 3.66 (s, 3 H, methoxyl), 3.59 (s, 3 H, methoxyl), 3.37 (t, J = 7 Hz, 2 H, C_5 H's), 3.15 (t, J = 7 Hz, 4 H, C_3 H's and NCH_2C), 2.31 (t, J = 7 Hz, 2 H, $-CH_2CO_2-$), 1.2–2.2 (m, 8