methyl]benzylamine (**29b**): bp 175 °C (14 mmHg); NMR ($CDCl_3$) δ 0.34 (s, 6 H, $SiCH_3$), 2.13 (s, 3 H, NCH_3), 2.16 (s, 2 H, $SiCH_2$), 3.40 (s, 2 H, $PhCH_2$), 7.00–7.65 (m, 10 H, aromatic H).

Acknowledgment. The authors gratefully thank the Shin-Etsu Chemical Industry Co., Ltd., for a generous gift of chlorosilanes.

Registry No. 8, 4525-48-8; **9a**, 18182-40-6; **9b**, 54926-29-3; **9c**, 54926-32-8; **9d**, 53174-43-9; **10a**, 72443-52-8; **10b**, 72443-53-9; **10c**, 72443-54-0; **10d**, 72443-55-1; **12a**, 72443-56-2; **12b**, 72443-57-3; **12c**, 72443-58-4; **12d**, 72443-59-5; **13a**, 41839-73-0; **13b**, 72443-60-8; **13c**, 72443-61-9; **13d**, 72443-62-0; **16**, 54848-55-4; **19**, 72443-63-1; **20**, 69321-60-4; **21**, 72443-64-2; **22d**, 72443-65-3; **24a**, 72443-66-4; **24b**, 72443-67-5; **24c**, 72443-68-6; **24d**, 72443-69-7; **26b**, 766-77-8; **26c**, 776-76-1; **26d**, 789-25-3; **27**, 1126-71-2; **28**, 103-83-3; **29a**, 51951-99-6; **29b**, 72443-70-0; [(dimethylamino)methyl] phenyl sulfide, 43180-39-8.

Aromatization of Dihydrothiophenes. Thiophenesaccharin: A Sweet Surprise[1,2]

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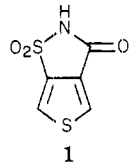
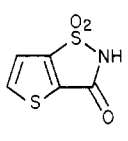
Received August 20, 1979

Sulfuryl choride has been shown to be highly effective in the dehydrogenation of 3,4-disubstituted-2,5-dihydrothiophenes and 2,3-disubstituted-4,5-dihydrothiophenes, in which the 3,4 and 2,3 substituents are part of a β-keto carbonyl functionality or its enol derivatives. Its use in the preparation of the key intermediate for the synthesis of the new artificial sweetener thiophenesaccharin is described.

In connection with the development of a new technically feasible synthesis of recently described new artificial sweetener thiophenesaccharins[3] [2,3-dihydro-3-oxothieno[3,4-*d*]isothiazole 1,1-dioxide (**1**), its [2,3-*d*] isomer (**2**), and its [3,2-*d*] isomer (**3**)], a mild, high-yield, operationally simple method for the aromatization of certain 3,4- and 2,3-disubstituted-dihydrothiophenes was required.



1



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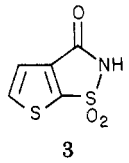


3

The literature-reported dehydrogenation reagents commonly used in thiophene synthesis are hydrogen peroxide,[4,5] perbenzoic acid,[5] phosphorus pentachloride,[3] chloranil,[6,10] selenium dioxide,[7] sulfur,[7] *N*-chlorosuccinimide,[8a] iodosobenzene,[5] nitrosobenzene,[7] and bromine.[9] Many problems have been encountered when these reagents have been used—difficulty in product isolation due to contamination with side products or reagent, long reaction times, high temperatures, and, in many cases, a large excess of a relatively expensive reagent is required with not always satisfactory results.

We have found sulfuryl chloride to be a highly efficient reagent for dehydrogenating, under mild conditions, 3,4-disubstituted-2,5-dihydrothiophenes (**4**) and 2,3-disubstituted-4,5-dihydrothiophenes (**6**), in which the 3,4 or 2,3 substituents are part of a β-keto carbonyl functionality or its enol ether derivative.[8b] Sulfuryl chloride has the advantage of being inexpensive and easy to handle, and any excess can be readily removed. The reaction is carried out by using 1–1.1 molar equiv of sulfuryl chloride and an appropriate solvent such as chloroform or methylene chloride at −10 to 0 °C. The reaction is complete within 1–2 h. The product is isolated by normal work-up procedures.

As shown in the tables, the yields are high and sensitive groups such as acetates, mesylates, thioethers, phosphates, esters, and ketones are not affected. In the aromatization of 3,4-disubstituted-2,5-dihydrothiophenes (**4a–4m**) the intermediate chloro compound spontaneously loses HCl and gives the thiophene. The intermediate chloro compounds in the 2,3-disubstituted cases (**6a–6j**) only partially lose HCl under the reaction conditions, and a base such as triethylamine is usually required to complete the reaction (see Experimental Section). The reaction can be easily scaled up without loss in yield or quality of product.

Sulfuryl chloride has been successfully used in the dehydrogenation of the key intermediates **8** (mp 182–186 °C) and **9** (mp 133–135 °C) for the syntheses of thiophenesaccharins **1** and **2** affording **10** (mp 92–95 °C) and

(1) Dedicated to Professor Dr. M. Seefelder on the occassion of his 60th birthday.

(2) Presented (in part) at the IVth International Congress of Pesticide Chemistry (IUPAC), Zürich, July 24–28, 1978.

(3) Hromatka, O.; Binder, D. Deutsche Offenlegungsschrift 2534689; *Chem. Abstr.* **1976**, *85*, 5612. The [3,4-*d*] isomer is 1000 times sweeter than sucrose and does not have the bitter metallic aftertaste characteristic of saccharin.

(4) (a) Stoll, A.; Süess, R. *Helv. Chim. Acta* **1974**, *57*, 2487. (b) Krieger, M.; Süess, R. U.S. Patent 3929833; *Chem. Abstr.* **1972**, *77*, 34295.

(5) Takaya, T.; Kosaka, S.; Otsuji, Y.; Imoti, E. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2086, 2582.

(6) Ruschig, H.; Meixner, W.; Alpermann, H. G. U.S. Patent 3445473; *Chem. Abstr.* **1967**, *67*, 21811.

(7) Kiehne, H. Deutsche Offenlegungsschrift 1945964; *Chem. Abstr.* **1971**, *74*, 141507.

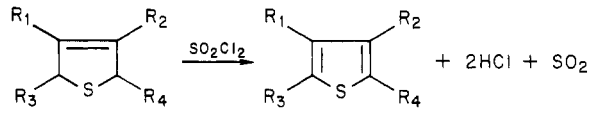
(8) (a) Safir, S. R. U.S. Patent 3953430; *Chem. Abstr.* **1972**, *85*, 33101. (b) Two recent papers published after the appearance of our patent applications (see also ref 2) mention the use of sulfuryl chloride in the oxidation of similar dihydrothiophenes, affording the corresponding thiophene derivatives: Press, J. B.; Safir, S. R., et al. *J. Med. Chem.* **1979**, *22*, 725. Press, J. B. et al. *J. Org. Chem.* **1979**, *44*, 3292.

(9) Ruschig, H.; Schorr, M.; Muschaweck, R.; Rippel, R. *Deutsche Auslegungsschrift* 1643325; *Chem. Abstr.* **1969**, *71*, 91287.

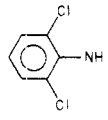
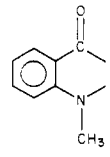
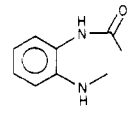
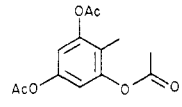
(10) Chakrabarti, J. K.; Tupper, D. Belgian Patent 835932; *Chem. Abstr.* **1977**, *86*, 29893.

0022-3263/80/1945-0617$01.00/0

Table I. 3,4-Disubstituted-2,5-dihydrothiophenes

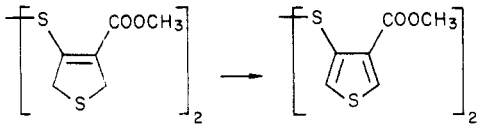


4

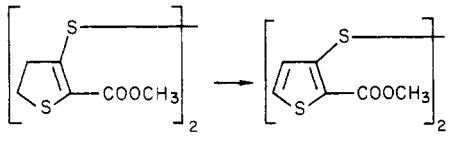
entry	substituent R_1	R_2	R_3	R_4	mp, °C/bp, °C (torr) 4	5	% yield[a]
a	OH	CO_2CH_3	H	H	38-41[c]	76-84 (0.07)[d]	85[b]
b	OH	CO_2CH_3	H	CH_3	72-75 (0.04)	67-70 (0.03)[d]	75
c	OCH_3	CO_2CH_3	H	H	79-81	66-67	93
d	OH	CN	H	H	70-72	oil	77
e	OH	$COCH_3$	H	H	119-121 (1.2)	40-43	80
f	$OCOCH_3$	$COOCH_3$	H	H	49-51	56-58	91
g	OSO_2CH_3	CN	H	H	80-82	52-55	88
h		CN	H	H	170-173[e]	105-108[e]	75
i			H	H	231-232[f]	188-190[f]	70
j			H	H	225-230[g]	237-239[g]	85
k			H	H	174-176[h]	149-155	95
l	PhS	CN	H	H	79-91	32-34	90
m	$(EtO)_2P(O)O$	$COOCH_3$	H	H	127-130 (0.3)	124-126 (0.2)	98

[a] All compounds exhibited satisfactory spectral and analytical data. [b] Reaction performed at room temperature to minimize formation of 2-chloro-3-hydroxy-4-(carbomethoxy)thiophene. [c] References 11 and 16. [d] Reference 12. [e] Reference 6. [f] Reference 13. [g] Reference 14. [h] Similar compounds are known in the literature. See ref 15.

11 (mp 141–143 °C), respectively. The remarkable stability of the disulfide linkage to further oxidation and the substituted thiophene to ring chlorination under the conditions used should be noted.



8 10



9 11

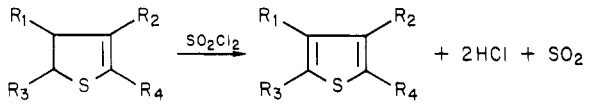
Because 1, as its sodium salt, is the sweetest of the three isomers, a technically feasible synthesis based on the above dehydrogenation reaction was worked out starting from readily available methyl thioglycolate and methyl acrylate (see Scheme I). The literature known preparations of methyl tetrahydro-4-oxothiophene-3-carboxylate (**12**)[13,16] yielded a mixture of isomers, 3,4- and 2,3-keto esters, which could not be easily separated by distillation or other physical means. By a simple modification of the reaction conditions and work-up procedure, a crystalline methyl tetrahydro-4-oxothiophene-3-carboxylate could be obtained with no contamination of the 2,3 isomer. Introduction of the disulfide group, aromatization, oxidative chlorination, treatment with ammonia and cyclization led directly to the sodium salt of thiophenesaccharin[19] (**16**) in an overall yield of 20%. The yields given in Scheme I are representative for a pilot plant scale production of thiophenesaccharin sodium salt. Studies in the field of applications research, mutagenicity, and toxicology should show whether these products could be used as commercial artificial sweeteners.

Experimental Section

Melting points were determined on a Buchi B510 melting point apparatus and are uncorrected. All reported compounds are homogeneous by thin-layer chromatography analysis [Merck 60

(11) Hromatka, O.; Binder, D.; Eichinger, K. *Monatsh. Chem.* **1973**, *104*, 1520.
(12) Courtin, A.; Class, E.; Erlenmeyer, H. *Helv. Chim. Acta* **1964**, *47*, 1748. Benery, E.; Baravian, A. *Ber. Dtsch. Chem. Ges.* **1915**, *48*, 593.
(13) Hromatka, O.; Binder, D.; Eichinger, K. *Monatsh. Chem.* **1974**, *105*, 1164.
(14) Hromatka, O.; Binder, D.; Eichinger, K. *Monatsh. Chem.* **1975**, *106*, 375, 555.
(15) Razdan, R. K.; Pars, H. G. Belgian Patent 755213; *Chem. Abstr.* **1971**, *74*, 125667.
(16) Woodward, R. B.; Eastmann, R. H. *J. Am. Chem. Soc.* **1946**, *68*, 2229.
(17) Fiesselmann, H. Deutsches Patent 1020641; *Chem. Abstr.* **1961**, *54*, 2357*b*.
(18) Pankiewicz, J.; Decrois, B.; Morel, J. *C. R. Acad. Sci., Ser. C* **1975**, *281*, 39.
(19) Rossy, P. A.; Hoffmann, W.; Müller, N. DOS 2615885 (*Chem. Abstr.* **1978**, *88*, 50641), 2700261 (*Ibid.* **1978**, *89*, 109060), 2700215 (*Ibid.* **1978**, *89*, 109062), 2700262 (*Ibid.* **1978**, *89*, 109061), and patents pending.

Table II. 2,3-Disubstituted-4,5-dihydrothiophenes

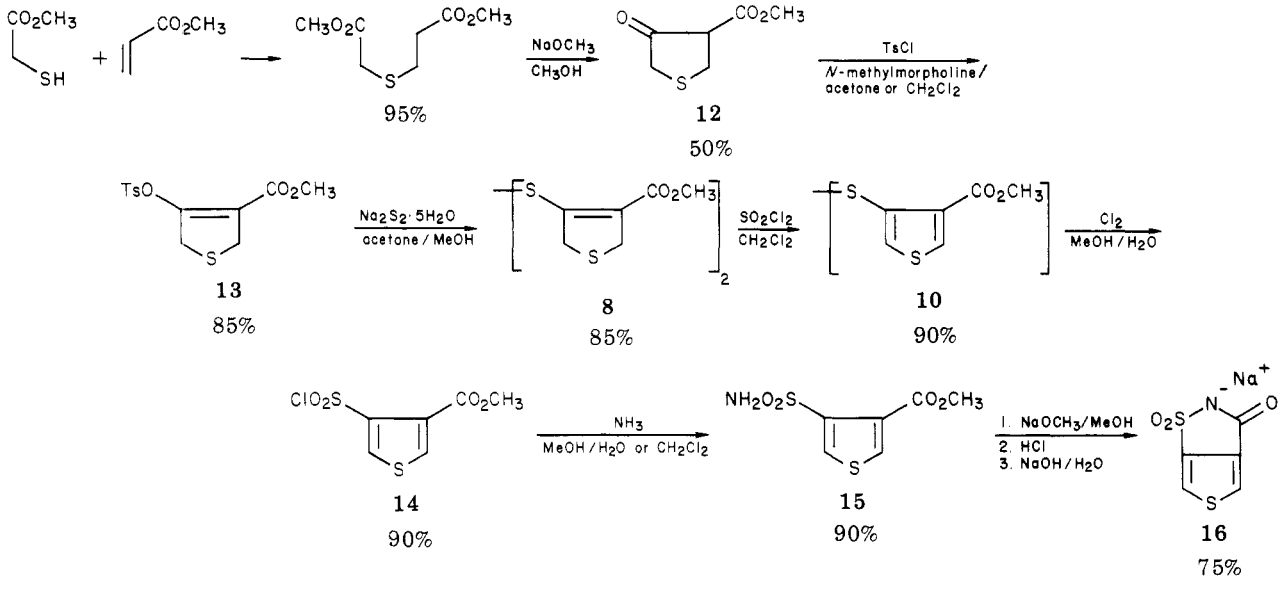


6 7

entry	substituent R_1	R_2	R_3	R_4	mp, °C/bp, °C (torr) 6	7	% isolated yield[a]
a	H	OH	H	$COOCH_3$	72-73 (0.1)[b]	68-73 (0.4)[c]	82
b	H	OH	CH_3	$COOCH_3$	72-75 (0.3)	67 (0.25)	75
c	H	OH	H	COPh	137-140 (0.1)	53-57	88
d	H	OH	H	CN	oil	88-92[d]	76
e	H	OCH_3	H	CN	82-83 (0.25)	72-74 (0.12)	91
f	H	$OCOCH_3$	H	$COOCH_3$	82-84 (0.06)	84-86 (0.03)	79
g	H	OSO_2CH_3	H	$COOCH_3$	75-77	oil	83
h	H	NH_2	H	COPh	147-149[e]	100-102[e]	77
i	H	$NHCOCH_3$	H	COPh	65-66[e]	93-95[e]	82
j	H	SPh	H	$COOCH_3$	43-45	63-66	93

[a] All compounds exhibited satisfactory spectral and analytical data. [b] Reference 16. [c] Reference 17. [d] Reference 18. [e] Reference 7.

Scheme I



F254 (5 × 20 cm) silica gel analytical plates]. ^1H NMR measurements were obtained on a Varian Associates A60D spectrometer and chemical shift values are reported in δ downfield from tetramethylsilane internal standard. IR spectra were recorded with a Perkin-Elmer 457 spectrometer.

The following preparative-scale experiments illustrate the aromatization procedure using sulfuryl chloride.

Methyl 4-Methoxythiophene-3-carboxylate (5c). To a stirred ice-cooled suspension of methyl 2,5-dihydro-4-methoxythiophene-3-carboxylate (**4c**, 174 g, 1 mol) in 1 L of methylene chloride was added sulfuryl chloride (89 mL, 1.1 equiv) during a period of 1 h. After a further reaction time of of 30 min the mixture was washed with 10% aqueous sodium bicarbonate solution (100 mL) and water (3 × 100 mL). The organic phase was separated and dried (sodium sulfate), and the solvent was removed under vacuum. The crude crystalline product was recrystallized from ether. A yield of 160 g (93%) was obtained: mp 66–67 °C; IR 1715 cm^{-1}; ^1H NMR δ 8.00 (d, 1 H, thiophene), 6.30 (d, 1 H, thiophene), 3.87 (d, 6 H, CH_3O). Anal. Calcd for $C_7H_8O_3S$: C, 48.78; H, 4.68; S, 18.62. Found: C, 49.13; H, 4.62; S, 18.15.

A similar procedure was used to prepare methyl 3-hydroxythiophene-2-carboxylate (**7a**) with the following modification. Thirty minutes after addition of sulfuryl chloride, water was added followed by triethylamine (1–2 molar equiv) at 0 °C until the pH of the aqueous solution was 7–8. The mixture was stirred for 1 h (after which time the pH of the aqueous solution was still ~7) and then worked up as above. A yield of 82% was obtained: bp 68–73 °C (0.4 torr); IR (neat) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.50 (s, 1 H), 7.30 (d, 1 H, thiophene), 6.65 (d, 1 H, thiophene), 3.81 (s, 3 H). Anal. Calcd for $C_6H_6O_3S$: C, 45.55; H, 3.82; S, 20.27. Found: C, 45.01; H, 3.79; S, 20.20.

The following procedures are representative for the preparation of thiophenesaccharin (1).

Methyl tetrahydro-4-oxothiophene-3-carboxylate (**12**) was prepared according to the procedure of Hromatka et al.[11] with the following workup modification. The reaction mixture was poured into ice–water, stirred for 30 min (the 2,3 isomer is not stable in aqueous base), and acidified with concentrated hydrochloric acid (~pH 2). The mixture was filtered and dried to afford the product as a white crystalline solid in a yield of 50–55%: mp 36–37 °C; IR (KBr) 1750, 1725, 1660, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.8 (m, 5 H), 3.4 (m, 3 H). According to the ^{13}C NMR spectrum the keto ester exists in solution as a 35/65 mixture of the keto and enol forms, respectively. Anal. Calcd for $C_6H_8O_3S$: C, 44.98; H, 5.03; S, 20.02. Found: C, 45.21; H, 5.26; S, 19.75.

Methyl 2,5-Dihydro-4-(*p*-toluenesulfonato)thiophene-3-carboxylate (13). Methyl tetrahydro-4-oxothiophene-3-carboxylate (160 g, 1 mol) and *N*-methylmorpholine (142 g, 1.4 equiv) were dissolved in methylene chloride (300 mL). *p*-Toluenesufonyl chloride (200.2 g, 1.05 equiv) and methylene chloride (300 mL) were added dropwise to the cooled solution (10 °C) over a period of 30 min. The mixture was stirred at this temperature for a further 1 h, the solution was washed with water and the organic phase was separated, dried (sodium sulfate), and concentrated. The crude product was recrystallized from cyclohexane or methanol to give 267 g (85%) of the title compound:

mp 91–92 °C; IR (KBr) 1695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.90 (d, 2 H, phenyl), 7.35 (d, 2 H, phenyl), 3.85 (m, 4 H), 3.60 (s, 3 H, CH_3O), 2.45 (s, 3 H). Anal. Calcd for $C_{13}H_{14}O_5S_2$: C, 49.66; H, 4.49; S, 20.40. Found: C, 49.62; H, 4.65; S, 20.25.

Dimethyl 4,4′-Dithiobis(2,5-dihydrothiophene-3-carboxylate) (8). A sodium disulfide solution, prepared by heating a mixture of sodium sulfide (~60% in water) (20.5 g, 0.16 mol), sulfur (5.01 g, 0.16 mol), and methanol (120 mL) for 1 h at 60 °C, was added over a 2-h period to an ice-cooled mixture of methyl 2,5-dihydro-4-(*p*-toluenesulfonato)thiophene-3-carboxylate (94.2 g, 0.3 mol) in acetone (450 mL). The mixture was stirred at 10 °C for a further 8 h and then poured into 450 mL of water. The precipitated product was filtered and washed with water (3 × 50 mL) and methanol (3 × 50 mL). Any starting tosylate or sulfur was removed from the crude product by extracting once with boiling acetone (200 mL) and once with boiling cyclohexane (200 mL) and then filtering and drying. A yield of 44.6 g (85%) of a colorless crystalline solid was obtained: mp 169–171 °C (toluene); IR (KBr) 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.15 (m, 8 H), 3.78 (s, 6 H). Anal. Calcd for $C_{12}H_{14}O_4S_2$: C, 41.12; H, 4.03; S, 36.59. Found: C, 41.25; H, 40.05; S, 36.60.

Dimethyl 4,4′-Dithiobis(thiophene-3-carboxylate) (10). Compound **8** (115.5 g, 0.33 mol) was suspended in methylene chloride (800 mL). To this mixture was added sulfuryl chloride (94.2 g, 1.06 equiv) in methylene chloride (800 mL) over a period of 1 h. After an additional reaction time of 1 h the mixture was washed with water and 10% aqueous sodium bicarbonate, and the organic phase was separated, dried, and concentrated to give 103 g (90%) of the title compound: mp 92–95 °C (methanol); IR (KBr) 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.15 (d, 1 H, thiophene), 7.25 (d, 1 H, thiophene), 3.90 (s, 3 H). Anal. Calcd for $C_{12}H_{10}O_4S_4$: C, 41.60; H, 2.91; S, 37.02. Found: C, 41.85; H, 3.00; S, 36.75.

Methyl 4-(Chlorosulfonyl)thiophene-3-carboxylate (14). Compound **10** (346 g, 1 mol) was dissolved in a mixture of methanol (2 L) and water (750 mL). The solution was cooled to 0 °C, chlorine gas (415 g, 5.85 mol, 1.17 equiv) was introduced during a period of 2–3 h, and the mixture was stirred a further 2 h. The mixture was poured into 3 L of ice–water and the precipitated product was filtered, dried, and recrystallized (carbon tetrachloride or methanol) to yield 433 g (90%): mp 70–72 °C; IR (KBr) 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.35 (d, 1 H, thiophene), 8.25 (d, 1 H, thiophene), 3.90 (s, 3 H). Anal. Calcd for $C_6H_5ClO_4S_2$: C, 29.94; H, 2.09; Cl, 14.73; S, 26.64. Found: C, 30.25; H, 2.32; Cl, 14.88; S, 26.55.

Methyl 4-Sulfamoylthiophene-3-carboxylate (15). Methyl 4-(chlorosulfonyl)thiophene-3-carboxylate (240.5 g, 1 mol) was dissolved in methylene chloride (2 L), the solution was cooled to 0 °C, and ammonia gas (51 g, 1.5 equiv) was introduced during a period of 2 h. After a further 2 h of stirring, the mixture was washed to neutrality with 10% aqueous hydrochloric acid and then with water (3 × 100 mL), and the organic phase was separated, dried (sodium sulfate), and concentrated. The crude product was recrystallized from ethanol to give 199 g (90%): mp 125–127 °C; IR (KBr) 1710 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 8.50 (d, 1 H, thiophene), 8.25 (d, 1 H, thiophene), 7.10 (s, 2 H, NH_2), 3.85 (s, 3 H). Anal. Calcd for $C_6H_7NO_4S_2$: C, 32.57; H, 3.19; N, 6.33; S, 28.98. Found: C, 32.58; H, 3.25; N, 6.29; S, 29.00.

2,3-Dihydro-3-oxothieno[3,4-*d*]isothiazole 1,1-Dioxide (1) Sodium Salt. A mixture of methyl 4-sulfamoyl-3-thiophenecarboxylate (33 g, 0.15 mol), methanol (150 mL), and a 30% methanolic solution of sodium methylate (34.9 g, 0.19 mol) was refluxed for 24 h. The mixture was cooled to ambient temperature and acidified with concentrated hydrochloric acid (18 mL, 0.22 mol), and the precipitated product was filtered and washed to neutrality with water. The product was dried and recrystallized from water to yield 23.4 g (83%): mp 250–252 °C; IR (KBr) 1725, 1690 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 11.30 (s, 1 H, NH), 8.62 (d, 1 H, thiophene), 8.50 (d, 1 H, thiophene). Anal. Calcd for $C_5H_3NO_3S_2$: C, 31.74; H, 1.60; N, 7.40; O, 25.37; S, 33.89. Found: C, 31.80; H, 1.79; N, 7.41; O, 25.63; S, 33.90.

The following procedure was used to convert the imide to its sodium salt monohydrate (**16**).

Thiophenesaccharin (23 g) was suspended in water (225 mL) and a 20% aqueous sodium hydroxide solution (20 mL) was added dropwise at 60 °C. A clear solution resulted after the mixture was heated at 80 °C for 1 h (pH 7.5–8). Activated charcoal (3 g) was added and the solution was filtered through a heated filter pad. The product was allowed to crystallize slowly. In this way 19 g of analytically pure sodium salt was obtained. Another 3 g of pure material was obtained by concentration of the mother liquors to 100 mL (total yield 80%). Anal. Calcd for $C_5H_4NO_4S_2Na$: C, 26.20; H, 1.76; N, 6.11; O, 27.92; S, 27.97; Na, 10.03. Found: C, 26.14; H, 1.79; N, 6.20; O, 28.21; S, 27.90; Na, 10.13.

Registry No. **1**, 59337-79-0; **4a**, 2689-68-1; **4b**, 65369-27-9; **4c**, 22097-91-2; **4d**, 16563-14-7; **4e**, 33348-85-5; **4f**, 65369-32-6; **4g**, 65369-23-5; **4h**, 16563-17-0; **4i**, 54968-46-6; **4j**, 56276-53-0; **4k**, 72228-76-3; **4l**, 65369-25-7; **4m**, 62303-30-4; **5a**, 70744-80-8; **5b**, 72228-77-4; **5c**, 65369-22-4; **5d**, 72228-78-5; **5e**, 72228-79-6; **5f**, 65369-31-5; **5g**, 65369-24-6; **5h**, 16563-34-1; **5i**, 54968-51-3; **5j**, 56276-58-5; **5k**, 72244-65-6; **5l**, 65369-26-8; **5m**, 72228-80-9; **6a**, 2689-69-2; **6b**, 67525-85-3; **6c**, 72228-81-0; **6d**, 72228-82-1; **6e**, 67525-90-0; **6f**, 67525-91-1; **6g**, 67525-92-2; **6h**, 31890-76-3; **6i**, 31890-77-4; **6j**, 67525-94-4; **7a**, 5118-06-9; **7b**, 5556-22-9; **7c**, 72228-83-2; **7d**, 57059-19-5; **7e**, 57059-18-4; **7f**, 16765-60-9; **7g**, 67525-93-3; **7h**, 30199-13-4; **7i**, 31968-31-7; **7j**, 67525-95-5; **8**, 67525-76-2; **10**, 67525-77-3; **13**, 67525-75-1; **14**, 59337-85-8; **15**, 59337-78-9; **16**, 67357-91-9; sulfuryl chloride, 7791-25-5; *p*-toluenesulfonyl chloride, 98-59-9.