above gave 80 mg (50%) of the (tricyanovinyl)thiazole **7** and 80 mg of unreacted thiazole **1a**.

(c) In Diethyl Ether. A solution of 500 mg (3.9 mmol) of TCNE in 600 mL of ethyl ether was added with stirring to an equivalent solution of thiazole **1a** in 20 mL of the same solvent. The color of the solution was initially deep blue, then turned to green, and finally, after 24 h, became red-brown; meanwhile, a gray precipitate was formed. After an additional 24 h, the precipitate was filtered, and we obtained 300 mg (26%) of 2-(dimethylamino)-1,3-thiazolium 1,1,2,3,3-pentacyanopropenide (**8a**): mp 105–107 °C (from dichloromethane–ethyl ether); IR (KBr) 2200 and 2190 (C≡N) cm^{-1}; ^1H NMR [$(CD_3)_2CO$] δ 3.46 (s, 6, NMe_2), 7.13 (d, 1, =CH), 7.5 (d, 1, =CH), 7.8 (br, 1, NH); ^{13}C NMR [$(CD_3)_2CO$] δ 42.6 (q, NMe_2), 56.7 (s, =C), 109.5 (d, =CH), 115.8 (s, C≡N), 116.8 (s, C≡N), 118.6 (s, C≡N), 128,2 (d, =CH), 159.8 (s, C=), 170.9 (s, $=CNMe_2$).

Anal. Calcd for $C_{13}H_9N_7S$: C, 52.87; H, 3.07; N, 33.20; S, 10.85. Found: C, 52.50; H, 2.95; N, 33.42; S, 11.0.

The filtrate was evaporated, and the residue was chromatographed (silica, 7:3 dichloromethane–ethyl acetate) to give 470 mg (53%) of the (tricyanovinyl)thiazole **7** and 100 mg of unreacted **1a**.

Reaction of 2-(Dimethylamino)-5-methyl-1,3-thiazole (1b) with Tetracyanoethylene (TCNE). (a) In Dichloromethane or Acetonitrile. A solution of 270 mg (2.1 mmol) of TCNE in 90 mL of solvent was added with stirring to an equivalent solution of thiazole **1b** in 30 mL of the same solvent. The reaction solution became initially green and then turned to brown. After 2 h half of the solvent was removed under vacuum, and an equal amount of ethyl ether was added. The resulting precipitate was filtered, and we obtained 160 mg (25%) of 2-(dimethylamino)-5-methyl-1,3-thiazolium 1,1,2,3,3-pentacyanopropenide (**8b**): mp 122–124 °C (from dichloromethane–ethyl ether); IR (KBr) 2220 and 2200 (C≡N) cm^{-1}; ^1H NMR [$(CD_3)_2CO$] δ 2.38 (d, 3, Me), 3.41 (s, 6, NMe_2), 7.2 (q, 1, =CH), 9.8 (br, 1, NH); ^{13}C NMR [$(CD_3)_2CO$] δ 12.1 (q, Me), 42.2 (q, NMe_2), 57.9 (s, =C), 114.2 (s, C≡N), 114.8 (s, C≡N), 117.1 (s, C≡N), 123.5 (s, =C), 124.1 (d, =CH), 136 (s, C=), 170.1 (s, $=CNMe_2$).

Anal. Calcd for $C_{14}H_{11}N_7S$: C, 54.35; H, 3.58; N, 31.69; S, 10.36. Found: C, 54.46; H, 3.68; N, 31.23; S, 10.62.

(b) In Diethyl Ether. A solution of 90 mg (0.70 mmol) of TCNE in 150 mL of solvent was added with stirring to an equivalent solution of thiazole **1b** (99.4 mg) in 20 mL of the same solvent. This resulted in immediate formation of a deep blue color which persisted for more than 1 h and then turned to yellow and finally to red-brown. After 4 days, the precipitate which formed was filtered and identified as the thiazolium salt **8b** (100 mg, 46%). Evaporation of the solvent and chromatography of the residue (silica, 1:1 dichloromethane–ethyl ether) gave 35 mg of unreacted thiazole **1b**.

From a reaction where the molar ratio between TCNE and **1b** was 2:1, the yield of **8b** was 75%.

From a reaction carried out with equivalent amounts of reactants (0.70 mmol) in ethyl ether distilled twice over Na wire was obtained the salt **8b** in ca. 30% yield after 10 days.

(c) In Methanol. A solution of 90 mg (0.78 mmol) of TCNE in 20 mL solvent was added with stirring to an equivalent solution of thiazole **1b** (99.4 mg) in 20 mL of the same solvent. After the mixture was allowed to stand for 24 h, the solvent was evaporated under vacuum, and the residue was crystallized from dichloromethane–ethyl ether to give 60 mg (29%) of 2-(dimethylamino)-5-methyl-1,3-thiazolium 2,2-dicyano-1-methoxy-1-oxoethenide (**9b**): mp 105–107 °C; IR (KBr) 2160 and 2190 (C≡N) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.35 (d, 3, Me), 3.36 (s, 6, NMe_2), 3.64 (s, 3, OMe), 7.01 (q, 1, =CH), 8.8 (broad, 1, NM); ^{13}C NMR ($CDCl_3$) δ 12.29 (q, Me), 33.15 (s, $C(CN)_2$), 42.40 (q, NMe_2), 51.28 (q, OMe), 121.37 (s, =C), 122.36 (s, C≡N), 124.25 (d, =CH), 169.08 and 173.48 (2, s, C=O and $=CNMe_2$.

Anal. Calcd for $C_{11}H_{14}N_4O_2S$: C, 49.61; H, 5.30; N, 21.04; S, 12.04. Found: C, 49.70; H, 5.28; N, 21.16; S, 11.94.

The NMR spectrum of the residue of crystallization showed the presence of unreacted thiazole **1b**.

Acknowledgment. We are grateful to Professor G. Gilli and Dr. V. Bertolasi, University of Ferrara, for providing us with the X-ray structural analysis of thiazolium salt **8b**. The continued financial support of Consiglio Nazionale delle Ricerche, Rome, is also gratefully acknowledged.

Registry No. 1a, 6142-08-1; **1b**, 52963-36-7; **2**, 77080-46-7; **3**, 77080-47-8; **4**, 77080-48-9; **7**, 77080-49-0; **8a**, 77097-70-2; **8b**, 77080-50-3; **9b**, 77080-51-4; tetracyanoethylene, 670-54-2; diethyl azodicarboxylate, 1972-28-7; *p*-toluenesulfonyl isocyanate, 4083-64-1; 4-azido-3-chloro-5-methoxy-2(5*H*)-furanone, 60010-88-0; 2-(dimethylamino)-*N*-methylthiazolium iodide, 31766-83-3; 2-(dimethylamino)-5-methyl-*N*-methylthiazolium iodide, 77080-52-5; chlorocyanoketene, 60010-89-1.

Convenient Synthesis of Unsymmetrical Aryl Sulfides

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In view of our interest in the role played by the substituents in the cleavage of the carbon–sulfur bond in aryl sulfides by means of electrophilic agents,[1] we required a variety of unsymmetrical aryl sulfides of general formula **1** (see Scheme I coupled with Table I), which were largely unknown.

Recent work by Fujisawa and co-workers[2] has shown that the iron-catalyzed *neat* sulfuration of a large excess of aromatic compound with arenesulfenyl chlorides (10:1 molar ratio) can provide a facile synthetic route for such compounds; however, under conditions similar to those reported, expensive and somewhat tedious procedures were required to isolate pure compounds.

We now report a simpler and more expeditious method than the previous one for preparing the required new unsymmetrical aryl sulfides in high yield. Equimolar amounts of arenesulfenyl chlorides **2a–d** and the appropriate aromatic compounds **3a–d** were reacted in nitroethane at room temperature, in a nitrogen atmosphere, according to Scheme I. The reactions proceeded smoothly with the release of hydrogen chloride and subsided within 0.5–1 h to afford the corresponding aryl sulfides **4–19** (Table I). In general, reactions occurred in the absence of catalyst (method A), with the exception of the reactions of arenesulfenyl chlorides **2a–d** with mesitylene **3a**, which were carried out in the presence of tin(IV) chloride as a catalyst (method B).

The choice of mild conditions (temperature and reaction time, absence of light, solvent, and nitrogen stream) is crucial to avoid or minimize disproportionation of sulfenyl chlorides and double sulfuration.[2] Furthermore, *isolation of the products is achieved by simply evaporating the solvent, followed by crystallization or distillation.*

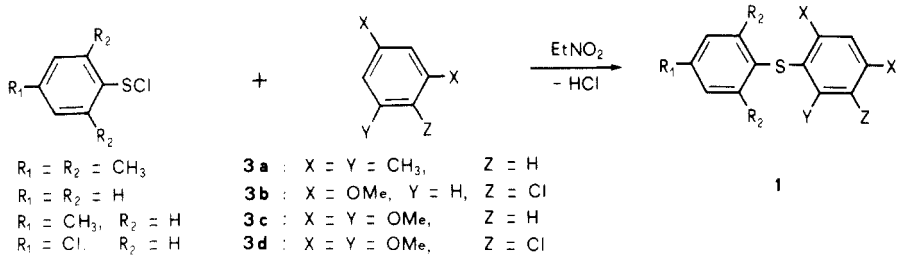
On the other hand, owing to decreased strength of (4-nitrophenyl)sulfenyl chloride as electrophilic agent,[2] sulfides **20–23**, bearing a nitro group in the para position, were prepared traditionally by nucleophilic condensation of *p*-nitrochlorobenzene with the appropriate potassium thiolate in refluxing ethanol (method C). The hitherto unreported 2,4,6-trimethoxythiophenol (**26**) and 3-chloro-2,4,6-trimethoxythiophenol (**27**) were prepared in

(1) F. Bottino and S. Pappalardo, *J. Chem. Soc., Perkin Trans. 1*, in press.

(2) T. Fujisawa, T. Kobori, N. Otsuka, and G. Tsuchihashi, *Tetrahedron Lett.*, 5071 (1968).

0022-3263/81/1946-2793$01.25/0

Scheme I

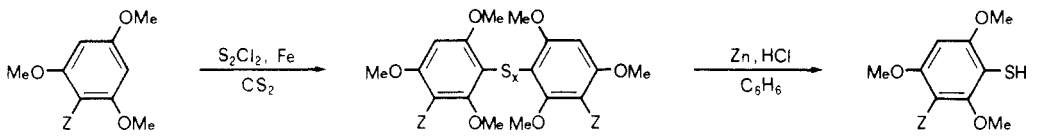


2a : $R_1 = R_2 = CH_3$
2b : $R_1 = R_2 = H$
2c : $R_1 = CH_3$, $R_2 = H$
2d : $R_1 = Cl$, $R_2 = H$

3a : $X = Y = CH_3$, $Z = H$
3b : $X = OMe$, $Y = H$, $Z = Cl$
3c : $X = Y = OMe$, $Z = H$
3d : $X = Y = OMe$, $Z = Cl$

1

Scheme II



3c : Z = H
3d : Z = Cl

24 : Z = H, x = 3
25 : Z = Cl, x = 2

26 : Z = H
27 : Z = Cl

Table I. Analytical and Physical Properties of Unsymmetrical Aryl Sulfides 4-23

compd	R_2	R_1	X	Y	Z	mp or bp, °C (mmHg)	method	yield, %	formula	mol wt	% sulfur calcd	% sulfur found
4	Me	Me	Me	Me	H	90-91[a]	B	82	$C_{18}H_{22}S$	270.4		
5	Me	Me	OMe	H	Cl	138-140	A	90	$C_{17}H_{19}ClO_2S$	322.8	9.93	9.89
6	Me	Me	OMe	OMe	H	113-114	A	78	$C_{18}H_{22}O_3S$	318.4	10.07	10.02
7	Me	Me	OMe	OMe	Cl	86.5-87.5	A	61	$C_{18}H_{21}ClO_3S$	352.8	9.09	9.13
8	H	H	Me	Me	H	120-122[b] (0.5)	B	84	$C_{15}H_{16}S$	228.3		
9	H	H	OMe	H	Cl	88-89	A	72	$C_{14}H_{13}ClO_2S$	280.7	11.42	11.40
10	H	H	OMe	OMe	H	122-123	A	75	$C_{15}H_{16}O_3S$	276.3	11.60	11.47
11	H	H	OMe	OMe	Cl	125-126	A	68	$C_{15}H_{15}ClO_3S$	310.8	10.32	10.39
12	H	Me	Me	Me	H	88-90	B	80	$C_{16}H_{18}S$	242.3	13.23	13.18
13	H	Me	OMe	H	Cl	92-94	A	85	$C_{15}H_{15}ClO_2S$	294.8	10.88	10.79
14	H	Me	OMe	OMe	H	119-120	A	71	$C_{16}H_{18}O_3S$	290.3	11.04	11.10
15	H	Me	OMe	OMe	Cl	104-105	A	65	$C_{16}H_{17}ClO_3S$	324.8	9.87	9.85
16	H	Cl	Me	Me	H	74-75	B	70	$C_{15}H_{15}ClS$	262.8	12.20	12.08
17	H	Cl	OMe	H	Cl	114-116	A	76	$C_{14}H_{12}Cl_2O_2S$	315.2	10.17	10.22
18	H	Cl	OMe	OMe	H	116-117.5	A	75	$C_{15}H_{15}ClO_3S$	310.8	10.32	10.25
19	H	Cl	OMe	OMe	Cl	118-119	A	65	$C_{15}H_{14}Cl_2O_3S$	345.2	9.29	9.23
20	H	NO_2	Me	Me	H	83-85	C	80	$C_{15}H_{15}NO_2S$	273.3	11.73	11.70
21	H	NO_2	OMe	H	Cl	165-167	C	82	$C_{14}H_{12}ClNO_4S$	325.7	9.84	9.76
22	H	NO_2	OMe	OMe	H	131-132	C	75	$C_{15}H_{15}NO_5S$	321.3	9.98	9.95
23	H	NO_2	OMe	OMe	Cl	150-152	C	78	$C_{15}H_{14}ClNO_5S$	355.8	9.01	9.05

[a] Lit. mp 90-91 °C: M. Yoshifuji, S. Tanaka, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **48**, 2607 (1975). [b] Lit. bp 176-177 °C (10 mm): G. Leandri, A. Mangini, and R. Passerini, *Gazz. Chim. Ital.*, **84**, 35 (1954).

good yields through a two-step synthesis by the iron-catalyzed sulfuration of *sym*-trimethoxybenzene (**3c**) and 2,4,6-trimethoxychlorobenzene (**3d**) with disulfur dichloride in carbon disulfide to give the corresponding trisulfide **24** and disulfide **25**, respectively, followed by reduction with zinc powder and hydrochloric acid in benzene,[3] as shown in Scheme II. The structure proof of compounds **24** and **25** was provided by comparison of their analytical and ^1H NMR spectral data with those of authentic samples, obtained by independent synthetic routes (see Experimental Section).

In our opinion, the introduction by this procedure of the mercaptide group into strongly activated substrates is recommended whenever standard procedures fail or lead invariably to complex mixtures of products.

Apart from analytical data, the identity of the compounds prepared is supported by their ^1H NMR spectra, which show appropriate integrals and the expected shifts for all protons. (See the paragraph at the end of the paper about supplementary material.) Analytical and physical properties of the sulfides **4-23** are listed in Table I.

Experimental Section

Melting points and boiling points are uncorrected. Elemental analyses were obtained commercially. ^1H NMR spectra were recorded on a Varian EM 360 spectrometer in $CDCl_3$ solutions with tetramethylsilane as an internal standard (δ 0). Arenesulfenyl chlorides **2b-d** were prepared by reaction of sulfuryl chloride with the appropriate thiol, according to the method described by Harpp and co-workers.[4] 2,4-Dimethoxychlorobenzene (**3b**) and 2,4,6-trimethoxychlorobenzene (**3d**) were prepared by literature procedures.[5] 2,4-Dimethoxy-5-chlorothiophenol was available from our previous work.[1] All experiments involving the preparation and use of sulfenyl chlorides were carried out in red glass flasks.

Mesitylsulfenyl Chloride (2a). To a mixture of thiomesitol[6] (3.04 g, 0.02 mol) and triethylamine (3 drops) in CCl_4 (30 mL), cooled at 0 °C, was added SO_2Cl_2 (2.83 g, 0.021 mol) in CCl_4 (30 mL) dropwise under stirring. After complete addition, the mixture was stirred at 0 °C for 0.5 h. Following removal of solvent under reduced pressure, orange-red crystals of the sulfenyl chloride were

(3) F. Bottino, S. Foti, and S. Pappalardo, *J. Chem. Soc. Perkin Trans. 1*, 1712 (1979).

(4) D. N. Harpp, B. T. Friedlander, and R. A. Smith, *Synthesis*, 181 (1979).

(5) G. Castelfranchi and G. Borra, *Ann. Chim. (Rome)*, **43**, 293 (1953).

(6) C. Wang and S. G. Cohen, *J. Am. Chem. Soc.*, **79**, 1924 (1957).

recovered in almost quantitative yield: bp 89–90 °C (0.5 mm), mp 40–43 °C [lit.[7] bp 95–101 °C (2.5–3.5 mm)]; NMR δ 2.33 (s, 3 H, Me), 2.65 (s, 6 H, Me), 7.03 (s, 2 H, aromatic H). Anal. Calcd for $C_9H_{11}ClS$: C, 57.89; H, 5.94; Cl, 18.99; S, 17.17. Found: C, 57.80; H, 5.91; Cl, 19.08; S, 17.12.

General Methods for Preparing Unsymmetrical Aryl Sulfides. The following procedures are typical of the methods used to prepared unsymmetrical aryl sulfides.

Method A. To a solution of the appropriate aromatic substrate (0.01 mol) in $EtNO_2$ (10 mL) was added an equimolar amount of arenesulfenyl chloride in $EtNO_2$ (10 mL) dropwise under N_2, with stirring. Stirring was continued until the evolution of HCl was complete (0.5–1 h). Removal of solvent under reduced pressure left crude crystals of the corresponding sulfide, which was recrystallized from ethanol to constant melting point (Table I).

Method B. A solution of arenesulfenyl chloride (0.01 mol) in $EtNO_2$ (10 mL) was added dropwise to a mixture of mesitylene (0.01 mol) and $SnCl_4$ (2 drops) in $EtNO_2$ (10 mL) under conditions identical to those described for method A. Workup consisted of removing the solvent in vacuo, washing the residue with a 1:1 ethanol–hydrochloric acid mixture (5 mL) and water, drying, and recrystallizing from ethanol. Only sulfide **8** was a liquid, which was purified by high-vacuum distillation (Table I).

Remarkably, in the attempt to prepare sulfide **6** by this procedure, **1,3-bis(mesitylthio)-2,4,6-trimethoxybenzene** [mp 174–175 °C (from ethanol)] was isolated as the major product: NMR δ 2.27 (s, 6 H, Me), 2.37 (s, 12 H, Me), 3.63 (s, 6 H, OMe), 3.74 (s, 3 H, OMe), 6.20 (s, 1 H, aromatic H), 6.90 (s, 4 H, aromatic H). Anal. Calcd for $C_{27}H_{32}O_3S_2$: C, 69.19; H, 6.88; S, 13.68. Found: C, 69.05; H, 6.85; S, 13.59.

Reaction of 3c with S_2Cl_2 To Produce Trisulfide 24. In a red glass flask, equipped with a magnetic stirring bar, a reflux condenser, an N_2 inlet, and a dropping funnel were placed a solution of **3c** (16.8 g, 0.1 mol) in CS_2 (40 mL) and iron powder (ca. 5 mg). The mixture was cooled at 0 °C, and under N_2 a solution of S_2Cl_2 (1.35 g, 0.01 mol) in CS_2 (10 mL) was added dropwise with stirring. Stirring was continued until the evolution of HCl was judged complete. After removal of solvent and subsequent steam distillation of the reaction mixture to remove the excess **3c**, a residue was left. It was extracted with $CHCl_3$, dried (Na_2SO_4), and concentrated under reduced pressure to give the trisulfide **24** (2.8 g, 65% yield) as a yellow crystalline powder, mp 176–177 °C (from AcOH). The analytical and spectral data of this product were identical with those of an authentic sample (see below).

2,4,6-Trimethoxythiophenol (26). To a stirred mixture of **24** (2.15 g, 5 mmol) and Zn powder (5 g) suspended in benzene (40 mL) and cooled in an ice-bath was added 37% HCl (50 mL) dropwise under stirring. When the addition of the acid was complete, the reaction mixture was stirred until the Zn had dissolved. The benzene layer was separated, washed with water, dried (Na_2SO_4), and concentrated under reduced pressure to give the desired thiol (1.6 g, 80% yield) as pale yellow prisms: mp 58–59 °C; NMR δ 3.75 (s, 1 H, SH), 3.79 (s, 3 H, OMe), 3.87 (s, 6 H, OMe), 6.15 (s, 1 H, aromatic H). Anal. Calcd for $C_9H_{12}O_3S$: C, 53.98; H, 6.04; S, 16.01. Found: C, 53.81; H, 6.02; S, 15.87.

Bis(2,4,6-trimethoxyphenyl) Trisulfide (24). A solution of SCl_2 (0.26 g, 2.5 mmol) in anhydrous Et_2O (20 mL) was added dropwise with stirring at 0 °C to a solution of thiol **26** (1 g, 5 mmol) in Et_2O (50 mL). The mixture was flushed with N_2 and stirred until the evolution of HCl subsided. The crude trisulfide **24** (1 g, 70% yield) was collected by filtration and recrystallized from AcOH to afford a yellow powder: mp 176–177 °C; NMR 3.87 (s, 6 H, OMe), 3.91 (s, 12 H, OMe), 6.17 (s, 4 H, aromatic H). Anal. Calcd for $C_{18}H_{22}O_6S_3$: C, 50.21; H, 5.15; S, 22.34. Found: C, 50.07; H, 5.09; S, 22.27.

Reaction of 3d with S_2Cl_2 To Produce Disulfide 25. Compound **3d** (16.16 g, 0.08 mol) and S_2Cl_2 (1.35 g, 0.01 mol) in CS_2 (100 mL) were reacted in the presence of catalytic amounts of iron powder under conditions identical with those described for the sulfuration of **3c**. On removal of the solvent, the residue was thoroughly washed with Et_2O to leave crude crystals of disulfide **25** (3.2 g, 68% yield) as yellow prisms, mp 196–198 °C (from AcOH). The analytical and spectral data of this product were identical with those of an authentic sample (see below).

3-Chloro-2,4,6-trimethoxythiophenol 27. This compound (mp 80–82 °C) was obtained in 87% yield by reduction of **25** with Zn and 37% HCl using a procedure identical with that followed for the preparation of thiol **26**: NMR δ 3.87 (s, 1 H, SH), 3.90 (s, 9 H, OMe), 6.35 (s, 1 H, aromatic H). Anal. Calcd for $C_9H_{11}ClO_3S$: C, 46.05; H, 4.72; Cl, 15.11; S, 13.66. Found: C, 45.84; H, 4.68; Cl, 15.24; S, 13.57.

Bis(3-chloro-2,4,6-trimethoxyphenyl) Disulfide (25). The thiol **27** (0.58 g, 2.5 mmol), dissolved in Me_2SO[8] (5 mL), was stirred for 24 h at room temperature. When the mixture was poured into brine, the disulfide precipitated in almost quantitative yield. It was collected by filtration, washed with water, and recrystallized from AcOH: mp 196–198 °C; NMR δ 3.77 (s, 12 H, OMe), 3.97 (s, 6 H, OMe), 6.35 (s, 2 H, aromatic H). Anal. Calcd for $C_{18}H_{20}Cl_2O_6S_2$: C, 46.25; H, 4.31; Cl, 15.17; S, 13.72. Found: C, 46.11; H, 4.30; Cl, 15.03; S, 13.64.

Method C. To a solution of *p*-nitrochlorobenzene (1.57 g) in EtOH (10 mL) was added an equimolar amount of the appropriate potassium thiolate dissolved in water (minimum amount) in one portion. The mixture was refluxed for 0.5 h and cooled. The precipitate obtained was collected by filtration, washed with water, dried, and recrystallized from EtOH to a constant melting point.

Registry No. 2a, 14575-12-3; **2b**, 931-59-9; **2c**, 933-00-6; **2d**, 933-01-7; **3a**, 108-67-8; **3b**, 7051-13-0; **3c**, 621-23-8; **3d**, 67827-56-9; **4**, 5324-71-0; **5**, 77189-83-4; **6**, 77189-84-5; **7**, 77189-85-6; **8**, 33667-80-0; **9**, 75787-00-7; **10**, 41280-62-0; **11**, 77189-86-7; **12**, 34678-74-5; **13**, 77189-87-8; **14**, 77189-88-9; **15**, 77189-89-0; **16**, 77189-90-3; **17**, 77189-91-4; **18**, 77189-92-5; **19**, 77189-93-6; **20**, 77189-94-7; **21**, 77210-79-8; **22**, 77189-95-8; **23**, 77189-96-9; **24**, 77189-97-0; **25**, 77189-98-1; **26**, 77189-99-2; **27**, 77190-00-2; 1,3-bis(mesitylthio)-2,4,6-trimethoxybenzene, 77190-01-3; *p*-nitrochlorobenzene, 100-00-5; potassium 2,4,6-trimethylthiophenol, 77190-02-4; potassium 3-chloro-4,6-dimethoxythiophenol, 77190-03-5; potassium 2,4,6-trimethoxythiophenol, 77190-04-6; potassium 3-chloro-2,4,6-trimethoxythiophenol, 77190-05-7; thiomesitol, 1541-10-2.

Supplementary Material Available: NMR spectral assignments for compounds **4-23** (1 page). Ordering information is given on any current masthead page.

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Formation and Fragmentation of 10-(Diethoxymethyl)-9-anthrone and Its Derivatives

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Carbonyl compounds, particularly those that are readily enolized, are commonly converted to their enol ethers by reaction with trialkyl orthoformates in the presence of acidic catalysts.[1,2] It seemed reasonable to expect that the reaction of anthrone with ortho esters would serve as a convenient and general synthesis of 9-alkoxyanthracenes. The acid-catalyzed reaction of anthrone with triethyl orthoformate was therefore examined.

Reaction of anthrone with a 1 molar equiv of triethyl orthoformate in the presence of sulfuric acid resulted principally in recovery of unchanged anthrone. Reaction

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(2) R. H. DeWolfe, "Carboxylic Ortho Acid Derivatives", Academic Press, New York, 1970.

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