with water and 1 M aqueous sodium hydroxide solution, followed by the aqueous washes described above in the general experimental section, affording 13.5 g (85%) of sulfide **2**, the physical and IR spectral properties of which were identical with those previously reported[10] for this same compound: bp 90 °C (bath temperature; 1.5 mm); NMR (CCl_4, Me_4Si) δ 7.19 (5 aromatic H's), 5.55 (m, 2 vinyl H's), 3.44 (complex m, CH_2S), 1.67 (br d, J = 5 Hz, vinyl CH_3). VPC analysis (oven temperature 170 °C, flow 15 mL/min) indicated the distilled product (retention time, 2.1 min) to be >98% pure.

(*E*)-9-(Phenylthio)-10-dodecen-1-ol (4). To a solution of 2.0 g (12.2 mmol) of crotyl phenyl sulfide (**2**), 2.0 g (9.6 mmol) of 8-bromo-1-octanol (**3**),[11] and approximately 50 mg of sodium iodide in 80 mL of anhydrous THF cooled to −70 °C (bath temperature) was added dropwise via syringe a solution of 24 mmol of lithium diisopropylamide[16] in 40 mL of 1:1 (v/v) anhydrous ether THF. This mixture was allowed to warm up to 5 °C over a period of 4 h, after which the reaction was quenched by addition of water. After removal of most of the solvent using a rotary evaporator under reduced pressure, the residue was diluted with 50 mL of solvent ether and washed in successive order with the aqueous solutions cited in the general experimental procedure. Since the crude product (3.37 g, >100% yield based on bromide **3**) could not be distilled without decomposition, it was chromatographed[17] on silica gel (150 mL, gradient elution using hexane–ether) to afford allylic sulfide **4** in 68% yield on the basis of bromo alcohol **3**: IR, ν_{max} (film) 3360 (OH), 1665, 1585, 1480, 1440, 1050, 1020, 955, 735, 685 cm^{-1}; NMR (CCl_4, Me_4Si) δ 7.28 (5 aromatic H's), 5.31 (m, 2 vinyl H's), 3.56 [3 H's, overlapping triplet (J = 6.5 Hz, CH_2OH) and multiplet (CHS)], 3.00 (s, OH), 1.61 (br d, J = 5 Hz, vinyl CH_3). Anal. Calcd. for $C_{18}H_{28}OS$: C, 73.92; H, 9.65; S, 10.96. Found: C, 73.92; H, 9.30; S, 10.79.

(*E*)-9-(Phenylsulfinyl)-10-dodecen-1-ol (5). To a solution of allylic sulfide **4** (11.5 mmol) in dichloromethane (100 mL) at 0 °C (bath temperature) was added in small portions over a period of several minutes 2.6 g of 85% *m*-chloroperbenzoic acid.[12] This mixture was subsequently stirred at 0 °C for 2 h, after which it was washed with 10% aqueous sodium carbonate and saturated brine. Removal of the organic solvent in the usual manner, followed by chromatography[17] on silica gel, afforded allylic sulfoxide **5** in quantitative yield: IR ν_{max} (film) 3440 (OH), 1665, 1585, 1445, 1375, 1305, 1145, 1080, 1035, 960, 775, 745, 685 cm^{-1}; NMR (CCl_4, Me_4Si) δ 7.53 (5 aromatic H's), 5.03–5.67 (complex pattern, 2 vinyl H's), 3.75 (s, OH), 3.3–3.7 (overlapping triplet and multiplet, CH_2OH and CHS), 1.1–1.8 (complex, 17 H). Anal. Calcd for $C_{18}H_{28}O_2S$: C, 70.08; H, 9.15; S, 10.39. Found: C, 70.23; H, 8.93; S, 10.02.

8(*E*),10(*E*)-Dodecadien-1-ol (6). A solution of allylic sulfoxide **5** (3.6 g, 11.7 mmol) and triethylamine (3.5 mL, 25 mmol) in 100 mL of toluene was heated at 80 °C (bath temperature) for 18 h. After this mixture was cooled to room temperature, it was washed in successive order with 5% aqueous hydrochloric acid, water, 5% aqueous sodium hydroxide, and saturated brine. Removal of the solvent in the usual manner, followed by chromatography on silica gel (50 mL, gradient elution using hexane–ether) and evaporative distillation [bp 135 °C (bath temperature), 3.0 mm], afforded 1.27 g (60%)[17] of dienol **6**, the IR and ^1H NMR spectral properties[13] of which were identical with those previously reported[15] for this pheromone. The chromatographed and distilled product was a low-melting solid (mp 25–30 °C) and was shown to be homogeneous by TLC and VPC analysis (oven temperature 150 °C; flow 15 mL/min; retention time, 5.3 min). ^{13}C NMR analysis,[14] however, revealed the presence of a small amount (<10%) of stereoisomeric impurities. The latter could be effectively removed after one recrystallization of this material from hexane at −5 °C, affording a stereochemically homogeneous sample of dienol **6**: mp 29–29.5 °C (lit.[15] mp 29–30 °C). The ^{13}C NMR spectrum exhibited by this material was fully consistent with the data recently reported[14] for an authentic sample of 8(*E*),10-(*E*)-dodecadien-1-ol (**6**).

Acknowledgment. We thank Dr. David S. Crumrine of Loyola University of Chicago for his assistance in determining the ^{13}C NMR spectrum of our synthetic pheromone.

Registry No. (*E*)-**1**, 29576-14-5; (*E*)-**2**, 36195-56-9; **3**, 50816-19-8; (*E*)-**4**, 83248-81-1; (*E*)-**5**, 83248-82-2; (*E*,*E*)-**6**, 33956-49-9; thiophenol, 108-98-5.

(16) This base was prepared by dropwise addition of a 1.2 M solution of methyllithium in ether (20 mL) to a solution of diisopropylamine (4.2 mL, 30 mmol) in 20 mL of anhydrous THF at −10 °C.

(17) Purification of intermediates **4** and **5** is not essential for the success of the overall synthetic sequence. 8-Bromo-1-octanol could be converted into dienol **6** in 33% overall yield (after chromatographic purification of the latter compound) with use of the crude product mixtures obtained in the preparation of **4** and **5**.

Synthesis of 4-Arylpyridines

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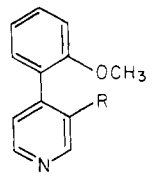
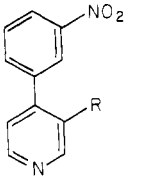
During the course of an investigation into intramolecular nucleophilic additions to pyridinium salts we required the 4-arylpyridines **1a** and **1b**.[1] We hoped to prepare these materials from the aromatic aldehydes and became attracted to the recent report of a preparation of **2a** and **2b** by modification of the Weiss procedure for pyridine synthesis.[2] The important feature of this new method is the



1a, R = H
b, R = CH_3



2a, R = H
b, R = CH_3

use of acylfurans **4** as the methylenic components in the condensation reaction with chalcones, leading to the isolation of the 2,6-difuryl-4-(3-nitrophenyl)pyridines. The furan moieties may be selectively oxidized to the diacids, which are readily decarboxylated to **2**. Furthermore, the preparation of the unsymmetrical pyridine **2b** is a distinct improvement over the original Chichibabin pyridine synthesis since α,β-unsaturated ketones were subject to reverse aldol reactions leading to product mixtures.[3] The principal drawback inherent in the Weiss procedure is the low yield of pyridine obtained since the intermediate dihydropyridine, formed in the initial stages of this reaction, aromatizes by the transfer of hydrogen to the chalcone.[4] This inefficient utilization of the aldehyde precursor prohibits the use of expensive or difficult to obtain aldehydes. In order to provide a satisfactory synthesis of 4-arylpyridines from the corresponding aldehydes, we investigated the simple and classical alternative to this procedure, which involves the preparation of 3-aryl-1,5-difuryl-1,5-pentanediones **5** and their reaction with hy-

(1) Weller, D. D.; Luellen, G. R. *Tetrahedron Lett.* **1981**, *22*, 4183.
(2) Carbateas, P. M.; Williams, G. L. *J. Heterocycl. Chem.* **1974**, *11*, 819.
(3) Frank, R. L.; Seven, R. P. *J. Am. Chem. Soc.* **1949**, *71*, 2629.
(4) Weiss, M. *J. Am. Chem. Soc.* **1952**, *74*, 200.

0022-3263/82/1947-4803$01.25/0

Scheme I

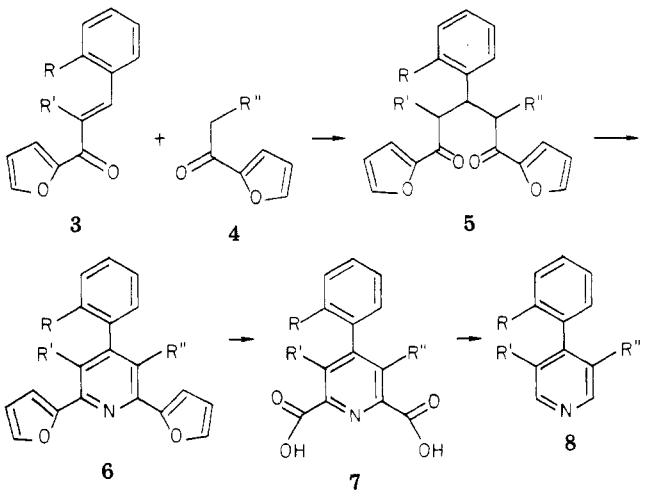


Table I. Preparation of 4-Arylpyridines

	trial			% yield			
	R	R'	R''	5	6	7[a]	8
a	OCH_3	H	H	93 (82)[b]	81	87	88
b	OCH_3	H	CH_3	99	71	90	83
c	H	H	H	(85)[c]	72	87	71
d	H	H	CH_3	97	68	90	63
e	H	H	CH_2CH_3	98	39	86	71
f	H	CH_3	CH_3	*d*	57[e]	91	61
g	H	CH_3	CH_2CH_3	*d*	20[e]	*f*	*f*
h	OCH_3	CH_3	CH_3				

[a] $KMnO_4$/acetone. [b] Yield directly from 2-methoxybenzaldehyde. [c] Yield directly from benzaldehyde. [d] Not purified; converted into **6**. [e] Yield from chalcone **3**. [f] These products were not obtained; see text.

droxylamine to give the pyridine **6**.[5,6]

The overall sequence of reactions is shown in Scheme I. The efficient Michael reaction allows for the production of both the symmetrical diketone **5a** and the unsymmetrical diketone **5b** (Table I). Diketone **5a** is also available directly from **3a** by combination aldol and Michael reactions. Experimentation revealed the Michael reaction to be irreversible under these conditions, since a mixture of excess acetylfuran and **5b** under the standard reaction conditions yields no other products, and a parallel experiment with **5a** and propionylfuran similarly determines that **5a** is stable to alcoholic base. Reaction of the diketones **5** with hydroxylamine hydrochloride in refluxing 1-butanol produces the corresponding pyridines in good yield. The formation of **6a,b** is accompanied by the appearance of considerable tar, which hinders the vacuum distillation of the difurylpyridine. The formation of tar is apparently due to acid-catalyzed decomposition of the furan rings in the product since addition of H_2SO_4 or HCl to the butanol reaction, or running the reaction in acetic acid, produces mainly tar. Unfortunately, addition of sodium acetate to neutralize liberated HCl causes the reaction to be very slow, with no increase in the amount of pyridine formed. The sensitivity of the furan rings is in contrast to the ease of pyridine formation observed with 1,5-diphenylpentanediones.[7] Oxidation of the furan rings in **6** is easily accomplished with use of potassium permanganate in acetone, producing the diacids **7** in high yield. Although efficient, the oxidation of the furyl groups with permanganate in acetone is inconvenient, since the optimal conditions call for portionwise addition of the oxidant over several days. A more practical procedure involves oxidation with permanganate in *tert*-butyl alcohol–water at 75 °C. After 12–18 h, a standard workup returns **7a** and **7b** in 95% and 70%, respectively.[9] Other oxidants, notably nitric acid[2] and ozone, give only small amounts of diacid **7a**. The decarboxylation of **7** to produce the pyridines **8** may be performed neat, but we prefer to employ Dowtherm or diphenyl ether. The overall yields for **8a** and **8b** from 2-methoxybenzaldehyde are 55% and 50%, respectively.[10]

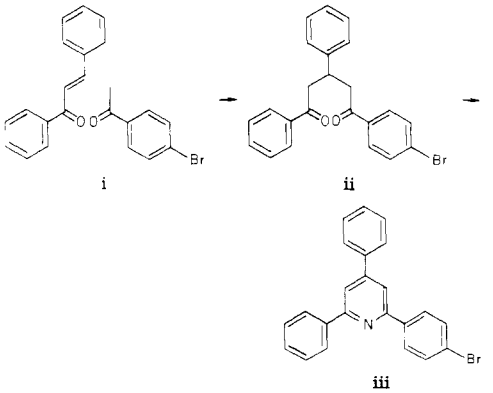
Although not required for our purposes, we prepared several additional pyridines (**8c–g**) to briefly examine the constraints on the reaction sequence.[12] Although the facile preparation of **8b,d** suggests the generality of obtaining the 3-alkylated pyridines, the formation of the 3-ethyl analogue **8c** is less successful. Here, the conversion of the oxime derivatives of **5c** to **6c** is very slow, leading to decomposition of the difurylpyridine. However, the subsequent oxidation and decarboxylation to give **8e** proceeded without difficulty. For the 3-alkylpyridine series then, a more acid stable aryl group is required to ensure product stability and allow more rapid pyridine ring formation via acid catalysis.

Preparation of the 4-aryl-3,5-dialkylpyridines is also more difficult. Formation of dialkyl diketones **5f** and **5g** is extremely slow under the usual conditions but proceeds to completion in concentrated sodium ethoxide in ethanol.[13] Only 110 mol % of acylfuran is employed since these diketones are thermally labile and excess ketone cannot be removed by distillation. The difficulty in the reaction of the alkyl chalcones is clearly illustrated by the observation that acetylfuran reacts with **3f** to yield only

(5) Stobbe, H. *Chem. Ber.* **1902**, *35*, 3978. Stobbe, H.; Volland, H. *Ibid.* **1902**, *35*, 3973. Stobbe, H.; Streigler, C. *J. Prakt. Chem.* **1912**, *86*, 241.

(6) For other recent 4-arylpyridine syntheses, see: (a) Katritzky, A. R.; Beltrami, H.; Sammes, M. *J. Chem. Soc., Perkin Trans 1* **1980**, 2480. (b) Harrison, E. A.; Rice, K. C.; Rogers, M. E. *Heterocycles* **1980**, *14*, 813. (c) Akiba, K-Y., Iseki, Y., Wada, M. *Tetrahedron Lett.* **1982**, *23*, 429.

(7) As an example, formation of the unsymmetrical pyridine iii proceeds cleanly (96%) under the usual reaction conditions. The overall yield of iii from chalcone i by this method (89%) is superior to the recent method of Tewari,[8] using isoquinolinium ylides for the preparation of iii (55%).



(8) Tewari, R. S.; Dubey, A. K. *J. Chem. Eng. Data.* **1980**, 2591.

(9) The diacids listed in Table I were produced by the $KMnO_4$/acetone procedure as described in the experimental section. When the oxidation of **6b** is performed under more concentrated conditions (1g of **6b** in 50 mL of acetone), with less $KMnO_4$ (110 mol %), and at a higher temperature (40 °C), the reaction is complete in 5 h and 83% of **7b** can be isolated.

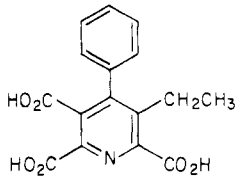
(10) The yield for **8b** is based upon a 95% yield for the formation of chalcone **3a**.[11] With the exception of the pyridine formation reaction, yields have not been optimized.

(11) Hanson, G. A. *Bull. Chim. Soc. Belg.* **1958**, *67*, 91.

(12) Full experimental details for the preparation of pyridines **8c–g** and their precursors are in the supplementary material.

(13) Abell, R. D. *J. Chem. Soc. Trans.* **1903**, *83*, 360.

41% of **5d** although this diketone is efficiently produced beginning with the unalkylated chalcone **3c**. Interestingly, the dimethyl diketone **5h** in the *o*-methoxyphenyl series could not be prepared. While the dimethyl diketone **5f** gives moderate yields in the pyridine synthesis, the reaction of hydroxylamine hydrochloride with the methyl ethyl diketone **5g** is, as expected, extremely slow. Pyridine **6f** may be successfully oxidized and decarboxylated to **8f** but permanganate oxidation of **6g** leads to oxidation of the ring methyl. The product obtained is presumably the triacid **9** although characterization is more convenient after decarboxylation to the nicotinic acid **10**. This example is



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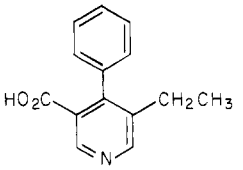

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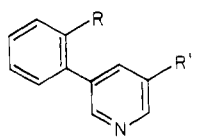
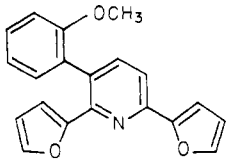
in distinct contrast to the previous examples and to the attempted oxidation of the side chain in **8b**, which is resistant to potassium permanganate in refluxing aqueous dioxane. Thus, except for the dimethyl case, this method does not appear to be applicable to the synthesis of 3,5-dialkylpyridines.

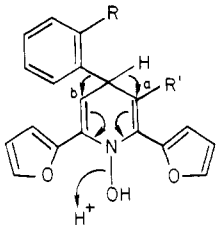
An additional limitation on the utility of this sequence became apparent when several samples of the 4-arylpyridines **8** were found to contain isomeric pyridines. In all cases, these products arose from difurylpyridines **6**, which, although distilled, were not recrystallized prior to the permanganate oxidation.[14] The minor isomer contaminating **8d** (10% by NMR) was isolated and characterized as 3-methyl-5-phenylpyridine (**11b**). That this isomer is formed during the pyridine ring closure step is supported by the isolation of **12** during the purification of large batches of **6a**. Oxidation and decarboxylation of **12** by the usual methods give pyridine **11a** as expected.



11a, R = OCH_3; R' = H
b, R = H; R' = CH_3



12



13

The identification of these pyridine isomers rests primarily on their ^{13}C NMR spectra, which reveal a protonated pyridine γ carbon, and on their ^1H NMR spectra, which show the expected patterns for the pyridine ring protons. The aryl migration to produce **12** can be accounted for by considering an intermediate dihydropyridine **13** formed from **5a** and hydroxylamine. This molecule can proceed to a pyridine by two pathways. The expected route, producing **6a** (path a), involves simple elimination of H_2O. In the minor pathway (path b) the loss of the hydroxyl function is accompanied by migration of the 4-aryl substituent, with subsequent loss of a proton from C-5, giving **12**.

(14) Pyridines **8d** and **8e** were found to be contaminated by ^1H NMR.

Experimental Section[15]

1,5-Di(2-furyl)-3-(2-methoxyphenyl)-2-methyl-1,5-pentanedione (5b). At 0 °C, 96.91 g (0.782 mol) of 2-propionylfuran[16] was added to a mixture of 35.64 g (0.156 mol) of **3a**[10,11] and 6.25 g (0.156 mol) of NaOH in 356 mL of CH_3OH. The reactants were stirred for 1 h at 0 °C and 40 h at 25 °C. The resulting solution was acidified with 1 N HCl and extracted with ether. The ether extracts were washed once with water and once with brine and then dried over $MgSO_4$. Ether was evaporated and excess 2-propionylfuran (62.81 g, 81% of theoretical) was recovered by Kugelrohr distillation [150 °C (1 mmHg)], leaving 54.23 g (99%) of **5b** as an amber-colored glass and as a mixture of stereoisomers: MS, m/z 352 (M^+), 243, 229, 211; ^1H NMR ($CDCl_3$, 100 MHz) δ 0.87 and 1.06 (each d, J = 7 Hz, total intensity 3 H; relative intensity 1.2:1), 2.91–4.26 (m, total intensity 4 H), 3.62 and 3.74 (each s, total intensity 3 H), 6.37–6.51 (m, total intensity 2 H), 6.63–7.60 (m, total intensity 8 H); IR (thin film) 3150, 1660, 1460, 1240, 740 cm^{-1}.

Anal. Calcd for $C_{21}H_{20}O_5$: M_r 352.132. Found: M_r 352.131.

2,6-Di(2-furyl)-4-(2-methoxyphenyl)-3-methylpyridine (6b). A mixture of 5.00 g (0.0142 mol) of diketone **5b** and 3.95 g (0.0568 mol) of hydroxylamine hydrochloride in 50 mL of *n*-butyl alcohol was heated at reflux for 6 h. Toluene (50 mL) and water (50 mL) were added, and the black reaction mixture was basified with 2 N NaOH. The aqueous layer was extracted twice more with toluene, and the combined extracts were washed with water and saturated brine and then dried over $MgSO_4$. The solvents were evaporated, the residue was dissolved in $CHCl_3$, and 20% by weight of silica gel was added. After standing, the silica gel was filtered off and $CHCl_3$ evaporated to give a thick, black tar. Kugelrohr distillation [150–190 °C (0.1–0.05 mmHg)] gave 3.32 g (71%) of **6b** as a glass, which crystallized from ethanol. An analytical sample was prepared by sublimation [110 °C (0.1 mmHg)]: mp 113–114 °C; MS, m/z 331 (M^+), 316, 302, 300, 242, 165; IR (KBr) 3110, 2960, 2940, 2840, 2750, 1600, 1490, 1250, 1020, 1010, 730 cm^{-1}; ^1H NMR ($CDCl_3$, 100 MHz) δ 2.30 (3 H, s), 3.76 (3 H, s), 6.45–6.56 (2 H, m), 6.92–7.60 (8 H, m), 7.48 (1 H, s).

Anal. Calcd for $C_{21}H_{17}NO_3$: M_r 331.121. Found: M_r 331.120.

4-(2-Methoxyphenyl)-3-methylpyridine-2,6-dicarboxylic Acid (7b). 1. $KMnO_4$/Acetone. To a solution of 4.00 g (0.0121 mol) of **6b** in 800 mL of acetone was added 5.73 g (0.0363 mol) of $KMnO_4$. While the mixture was vigorously stirred at 25 °C, an additional 22.92 g of $KMnO_4$ was added, in four identical portions (5.73 g, 0.0363 mol) as the previous portion was consumed, over a period of 4 days. Water (400 mL) was then added and the contents of the reaction flask stirred for 1 h. Manganese dioxide was removed by suction filtration, washed with water, and filtered again. Acetone was then evaporated from the combined filtrates, and subsequent ether extraction of the basic solution removed unreacted starting material. The aqueous solution was acidified with 30% H_2SO_4 and extracted three times with ether. The combined extracts were washed with brine and dried over $MgSO_4$. Ether was evaporated and the resulting yellow oil solidified under vacuum, giving 3.11 g (90%) of **7b**: mp 173–184 °C dec; MS, m/z 287 (M^+), 243, 199; ^1H NMR (Me_2SO-d_6, 100 MHz) δ 1.55 (3 H, s), 4.08 (3 H, s), 7.10–7.92 (4 H, m), 8.14 (1 H, s); IR (KBr) 1720, 1600, 1250 cm^{-1}.

(15) Low-resolution mass spectra were obtained on a Varian MAT CH-7 mass spectrometer. High-resolution mass spectra and combustion analyses were performed by Richard Weilesek at the University of Oregon Micro-Analytical Lab. Proton NMR analyses were performed on Varian spectrometers, Models HA-100, FT-80, and EM-360, and carbon NMR analyses were performed on the FT-80 spectrometer. Chemical Shifts (δ) are reported as parts per million downfield from tetramethylsilane for proton spectra, while carbon spectra are referenced to the residual solvent signal. Infrared spectra were recorded on Perkin-Elmer Model 727B and 137 infrared spectrophotometers. Melting points were determined on a Büchi capillary melting point apparatus and are uncorrected.

(16) Heid, J. V.; Levine, R. *J. Org. Chem.* **1948**, *13*, 409.

2. $KMnO_4/t$-BuOH/H_2O. A mixture of 1.00 g (3.02 mmol) of **6b**, 200 mL of *tert*-butyl and 40 mL of water was heated to 75–80 °C, and potassium permanganate (6.19 g, 0.0392 mol) was then added. After 17 h, the solution was filtered while hot to remove MnO_2, and a 20% t-BuOH/H_2O mixture was used to wash the solid well. Enough aqueous $NaHSO_3$ was added to the filtrate to destroy any residual MnO_2. Solvents were evaporated until a minimum amount of water remained. When the aqueous solution was acidified with 2 N HCl, **7b** precipitated as a yellow solid, 0.61 g (70%).

4-(2-Methoxyphenyl)-3-methylpyridine (8b). In 36 mL of diphenyl ether, 7.28 g (0.0254 mol) of **7b** was heated at 220 °C until CO_2 evolution was complete. The dark-brown solution was taken up in diethyl ether and then extracted four times with 3 N HCl. The resulting aqueous solution was backwashed with diethyl ether and then brought to pH 9 with concentrated NH_4OH. The basic solution was extracted three times with CH_2Cl_2. The combined extracts were washed with water and brine and then dried over $MgSO_4$. Solvent was evaporated and the resulting crude oil was distilled by Kugelrohr [100–130 °C (0.2 mmHg)] to give 4.20 g (83%) of **8b** as a clear oil: MS, m/z 199 (M^+), 184, 168; ^1H NMR ($CDCl_3$, 100 MHz) δ 2.12 (3 H, s), 3.74 (3 H, s), 6.93–7.46 (5 H, m), 8.43 (1 H, d, J = 5 Hz), 8.46 (1 H, s); IR (thin film) 2970, 2840, 1600, 1480, 1270, 1240, 750 cm^{-1}.

Anal. Calcd for $C_{13}H_{13}NO$: M_r 199.100. Found: M_r 199.100.

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Supplementary Material Available: Full experimental data for the preparation of **8a,c–g**, **9**, **10**, **11a,b**, **12** (13 pages). Ordering information is given on any current masthead page.

Reduction of Sulfonyl Halides with Iodotrimethylsilane: New Observations[1]

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Sulfonyl chlorides are easily and efficiently prepared by the chlorosulfonation reaction of arenes and alkanes.[2] For this reason their conversion to other organic sulfur compounds, in which the sulfur atom has a lower oxidation state, is of great synthetic value. Since organic disulfides are valuable starting materials for the synthesis of a variety of sulfenyl[3] and sulfinyl[4] compounds, the reductive coupling of sulfonyl chlorides to the corresponding disulfides constitutes an important process.

Table I. Reduction of Sulfonyl Halides and Related Compounds with Iodotrimethylsilane (1)

entry	reduced compd	% yield of disulfide	
1	$PhSO_2Cl$	94	95[a]
2	p-$CH_3C_6H_4SO_2Cl$	95	80[a]
3	o-$CH_3C_6H_4SO_2Cl$	95[b]	94[a,b]
4	2,4,6-$Me_3C_6H_2SO_2Cl$	80[b]	77[a,b]
5	2,4,6-i-$Pr_3C_6H_2SO_2Cl$	85[b,c]	
6	$PhSO_2I$	97	
7	$PhSO_2F$	97	
8	$PhSO_2SPh$	97.5	
9	$PhSO_2SMe$	mixture of disulfides	
10	PhS(O)SPh	98	96[a]
11	p-$CH_3C_6H_4S(O)SC_6H_4$-p-CH_3		96[a]
12	$CH_3S(O)SPh$	mixture of disulfides	
13	$PhSOCH_3$	96	

[a] Me_3SiCl/NaI in CH_2Cl_2 or benzene. [b] Compounds not obtained in a pure form after short-column chromatography. [c] This disulfide appeared to decompose partially during storage; it was purified by preparative TLC with hexane as a developing solvent (mp 82–87 °C) and analyzed by MS: m/e 470 (M^+), 235 (i-$Pr_3C_6H_2S^+$), 193 (i-$Pr_3C_6H_2^+$). However, its elemental analysis was not fully correct.

A recent report of Olah et al.[5] on the synthesis of disulfides from sulfonyl halides using iodotrimethylsilane as a reducing agent prompted us to publish the results of our independent studies on the synthetic and mechanistic aspects of this reaction which in some important details are different from those described by the above-quoted authors.

Thus, we have found that the reaction between sulfonyl chlorides and iodotrimethylsilane (1) in methylene chloride solution proceeds smoothly at room temperature within minutes (in some cases, hours), giving the corresponding disulfides **2** in high yields together with iodine, chlorotrimethylsilane, and hexamethyldisiloxane.

$$2RSO_2Cl + 10Me_3SiI \rightarrow RSSR + 5I_2 + 2\,Me_3SiCl + 4Me_3SiOSiMe_3$$

The reduction of sulfonyl halides can also be carried out with chlorotrimethylsilane in an inert solvent (benzene, chloroform, methylene chloride) and a suspension of sodium iodide even in the absence of a phase-transfer catalyst. In this case, however, the reaction requires a much longer time and a higher temperature especially for sterically hindered compounds. The results obtained are summarized in Table I.

However, in contrast to the report of Olah et al.,[5] we were able to detect the reaction intermediates formed during the reduction. Moreover, by means of the preparative TLC we succeeded in isolating these intermediates, which appeared to be the corresponding thiosulfonates **9**. It was also found that they are transiently formed not only during the reaction of **1** with sulfonyl chlorides and iodides but also with sulfinyl chlorides and alkyl sulfinates and that they disappear when the reduction is completed. Furthermore, in an independent experiment it was demonstrated that thiolsulfonates **9** are easily reduced by **1** to disulfides **2** at room temperature. These observations clearly demonstrate that thiolsulfonates **9** lie on the re-

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