and evaporated to give 80 mg (9.4%) of the starting material **5**. The acidic aqueous portion was adjusted to pH 10 with solid NaOH and was extracted with 5 × 15 mL of ether. The ether layers were combined, dried with $MgSO_4$, and evaporated to give a brown semisolid mass. Trituration with ether (10 mL) provided 570 mg (66.8%) of an off-white solid. LC (Partisil 10/25, 25 cm × 4.6 mm column, methanol, flow rate = 5 mL/min) afforded separation into two components. A 147-mg sample was dissolved in 0.3 mL of CH_3OH and injected onto the column in 10-μL portions; collecting and evaporating the fractions yielded 141 mg of **6**: retention time 9.8 min; mp 101–102 °C; IR (KBr) 3355, 3290, 3075 (br), 3030 (sh), 2955, 2875, 2855 (sh), 1595, 1485, 1450, 1365, 1320, 1260, 1215, 1190, 1165, 1140, 1115, 1090, 1065, 1005, 980, 970 (sh), 935, 905, 755, and 725 cm^{-1}; NMR ($CDCl_3$) δ 6.90–7.50 (m, 4, aromatic), 4.03 (s, 1, methine), 2.97–3.15 (m, 1, bridgehead), and 0.80–2.38 (m, 6, aliphatic); mass spectrum *m/e* (rel intensity) 190 (M + 1, 7), 189 (M^+, 47), 188 (17), 173 (12), 172 (91), 171 (8), 157 (7), 145 (9), 144 (24), 143 (14), 133 (11), 132 (100), 131 (16), 130 (55), 129 (34), 128 (45), 127 (8), 118 (9), 117 (38), 116 (29), 115 (54), 103 (9), 92 (11), 91 (9), 90 (5), 89 (7), 77 (12), 65 (7), 51 (7). Anal. Calcd for $C_{12}H_{15}NO$: C, 76.15; H, 7.99; N, 7.40. Found: C, 76.37; H, 8.04; N, 7.39.

Dry HCl gas was passed over the surface of a solution of **6** in ether. The solid product, **6**·HCl, was collected by filtration. Recrystallization from isopropyl alcohol gave crystals (mp 257 °C) suitable for X-ray analysis: IR (KBr) 3270, 3190, 3035, 2975 (sh), 2950, 2840, 2665 (sh), 2605 (sh), 1630, 1595, 1510, 1490 (sh), 1465 (sh), 1445, 1355, 1305, 1260, 1250, 1200, 1070, 765, and 725 cm^{-1}.

LC also provided 4.8 mg of an unidentified amine with a retention time of 16.9 min; its hydrochloride had mp 220 °C dec.

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Registry No.—**1**, 4428-22-2; **2**, 66792-54-9; **3**, 66792-55-0; **4**, 66792-51-6; **5**, 66792-52-7; **6**, 66808-36-4; **6** HCl, 66279-25-2; **8**, 66792-53-8; 1,2-naphthalenediol, 574-00-5; 1,2-naphthoquinone, 524-42-5; maleic anhydride, 108-31-6.

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Use of the Trimethylsilyl Group in Synthesis. Preparation of Sulfinate Esters and Unsymmetrical Disulfides[1a]

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Alkoxytrimethylsilanes and sulfinyl chlorides have been shown to couple efficiently to afford sulfinate esters; kinetic data indicate that a nonionic transition state is involved. The parallel reaction between aralkylthiotrimethylsilanes and sulfenyl chlorides gives unsymmetrical disulfides. An attempt to prepare sulfenate esters by the reaction of a sulfenyl chloride and an alkoxytrimethylsilane gave no reaction; in fact, sulfenate esters were shown to be cleaved by either chlorotrimethylsilane or trimethylsilyl cyanide to yield sulfenyl chlorides or thiocyanates, respectively. The reaction of *tert*-butyl hypochlorite with an alkylthiosilane gave disulfide.

A variety of silicon derivatives have seen widespread and growing use in the past few years[2] as protective groups and synthetic mediators. For instance, it is well known[2h,3] that acid chlorides react smoothly with alkoxysilanes to produce esters in good yield. Heteroatom analogues of this reaction could be of great utility; however, incomplete synthetic information and virtually no detailed mechanistic data are available for this reaction class[2h,4] (eq 1), which in principle encompasses

$$\mathrm{RC(=O)Cl + (CH_3)_3SiOR' \longrightarrow RC(=O)OR' + (CH_3)_3SiCl}$$

an impressive number of important functionalities. We wish to report on two facile syntheses using the trimethylsilyl group.

$$\mathrm{RXCl + (CH_3)_3SiYR' \rightarrow RXYR' + (CH_3)_3SiCl} \quad (1)$$

X = O, NR, S, S=O, PR, P(=O)R; Y = O, NR, S

When sulfinyl chlorides are treated with aralkoxytrimethylsilanes (eq 2), sulfinate esters (1) are cleanly produced in very good yield (Table I).[6]

$$\mathrm{RS(=O)Cl + R'OSi(CH_3)_3 \longrightarrow \underset{\mathbf{1}}{RS(=O)OR'} + (CH_3)_3SiCl} \quad (2)$$

R' = R = aralkyl

The precursor alcohols may be conveniently silylated[7] with hexamethyldisilazane using imidazole as catalyst. One equivalent of the alkoxytrimethylsilane is added to an equivalent of a sulfinyl chloride and the reaction is allowed to proceed at room temperature. The progress of the reactions may be conveniently followed by ^1H NMR spectroscopy, the singlet for chlorotrimethylsilane increasing at the expense of the peak for the trimethylsilyl group of the alkoxytrimethylsilane. Chlorotrimethylsilane may be easily removed by

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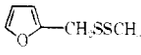
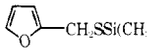
Table I. Preparation of Sulfinate Esters

sulfinate ester (1)	registry no.	yield, %	bp (torr) [mp], °C	n_D^{22}	ρ_{22}
(a) $CH_3S(O)OC_2H_5$	819-75-0	81	85–87 (80)[a]	1.4357[a]	
(b) $CH_3S(O)OCH_2C_6H_5$	35896-44-7	88	105–106 (1.5)[b]	1.5412[b]	1.164
(c) $C_6H_5S(O)OC_2H_5$	1859-03-6	83	87–88 (0.5)[c]	1.5351[c]	1.148
(d) $C_6H_5S(O)OCH_2C_6H_5$	29624-04-2	95	150 (0.025)[d]	1.5888[d]	1.148
(e) $C_6H_5CH_2S(O)OC_2H_5$	42300-72-1	54	83–84 (0.25)[e]	1.5370[e]	
(f) $C_6H_5CH_2S(O)OCH_2C_6H_5$	3358-25-6	48	[49–50][f]		

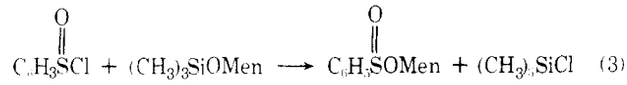
[a] Lit.[5a] 57–58 °C (25 Torr); n_D^{25} 1.4333. [b] Lit.[5b] 105 °C (0.03 Torr); n_D^{20} 1.5380. [c] Lit.[5c] 64–65 (0.06 Torr); n_D^{20} 1.5370. [d] Lit.[5b] 135–137 °C (0.05 Torr); n_D^{18} 1.5887. [e] Lit.[5d] 69–71 °C (0.025 Torr); n_D^{22} 1.5362. [f] Lit.[5e] 51–52 °C.

Table II. Preparation of Unsymmetrical Disulfides

disulfide (5)	registry no.	silyl thioether used	registry no.	yield, %	bp (torr) [mp], °C	n_D^{23}
(a) $C_6H_5CH_2SSC_6H_4$-CH_3-p	16601-19-7	$C_6H_5CH_2SSi(CH_3)_3$	14629-67-5	85	[33–34][a]	
(b) $C_6H_5SSC_3H_7$	20126-55-0	$C_3H_7SSi(CH_3)_3$	18143-79-8	67	71–73 (0.1)[b]	1.5838
(c) $C_6H_5SSC_3H_7$		$C_6H_5SSi(CH_3)_3$	4551-15-9	87	71–73 (0.1)[b]	1.5840
(d) $C_6H_5CH_2SSC_2H_5$	21230-16-0	$C_6H_5CH_2SSi(CH_3)_3$		86	69–71 (0.2)[c]	1.5841
(e) p-$CH_3C_6H_4SSC_6H_5$	29627-34-7	$C_6H_5SSi(CH_3)_3$		*d*		
(f) 	57500-00-2		1578-37-6	80	60–61 (0.8)	1.5661

[a] Lit.[12a] 34–35 °C. [b] Lit.[11f] 87–93 °C (0.1 Torr). [c] Lit.[12b] 75 °C (0.1 Torr). [d] 1:2:1 mixture by GLC.[13]

rotary evaporation. One useful application of this reaction involves the synthesis of menthylsulfinates, precursors of chiral sulfoxides.[8] By combining benzenesulfinyl chloride (**2**) and neat menthoxytrimethylsilane (**3**) the crude diastereomeric (**4**) mixture was obtained in 91% yield (eq 3). Crystal-



$$C_6H_5\overset{\overset{O}{\|}}{S}Cl + (CH_3)_3SiOMen \longrightarrow C_6H_5\overset{\overset{O}{\|}}{S}OMen + (CH_3)_3SiCl \quad (3)$$

2 3 4

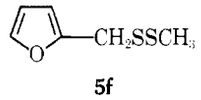
lization of the product from methanol gave the desired diastereomer in over 95% optical purity.[9] This approach should be useful in those cases where simple methoxide displacement on the sulfinyl chloride is ineffective.

We reasoned that other sulfur halides, such as sulfenyl chlorides, should be reactive toward alkylthiotrimethylsilanes.[10]

$$R'SCl + RSSi(CH_3)_3 \rightarrow R'SSR + (CH_3)_3SiCl \quad (4)$$

This was realized in that a variety of unsymmetrical disulfides **5**[10] were prepared in isolated yields averaging over 80% (Table II). In aralkyl and dialkyl cases only trace amounts of the symmetrical moieties are produced.[13] In a typical procedure a CCl_4 solution of the sulfenyl chloride (prepared in situ) is added dropwise to the alkylthiotrimethylsilane at 0 °C. The rapid discharge of the color of the sulfenyl chloride is used to monitor the reaction. After isolation of the product disulfide, no trace of the symmetrical disulfide was noted by TLC.

Of special interest was the synthesis of the mixed disulfide **5f**, reported to be a prime odor constituent of freshly baked



5f

bread.[14] We prepared this compound by the silicon exchange reaction using furfurylthiotrimethylsilane and methanesulfenyl chloride. It was also prepared by the sulfenimide route[11f,g] from either *N*-(methylthio)phthalimide or *N*-(methylthio)succinimide and furfuryl mercaptan. In each of the three syntheses a colorless liquid was obtained in ~75% yield. Gas chromatographic analysis, TLC, and MS revealed a single substance in each case under conditions which would have revealed the symmetrical species. In no case, under a variety of evaluation conditions, did the odor of the unsymmetrical species even remotely resemble the smell of baked bread. The spectral properties of our product appear to agree well with the published data; however, the disagreement as to the odor pinpoints the difficulty in evaluation of problems of this kind, particularly when the target compounds can undergo disproportionation readily.

Of considerable interest would be an effective synthetic route to sulfenate esters **6**.

RSOR

6

While the reaction of arylsulfenyl chlorides with alkoxide gives the desired ArSOR,[15] no general, reproducible technique is available for the preparation of the dialiphatic derivatives. When various alkoxytrimethylsilanes were reacted with arylsulfenyl chlorides, only starting materials were isolated.[16] In contrast, the reverse reaction involving treatment of methyl benzenesulfenate or *o*-nitrobenzenesulfenate with trimethylchlorosilane gave the corresponding sulfenyl chlorides.[17]

$$ArSOCH_3 + ClSi(CH_3)_3 \rightarrow ArSCl + CH_3OSi(CH_3)_3$$

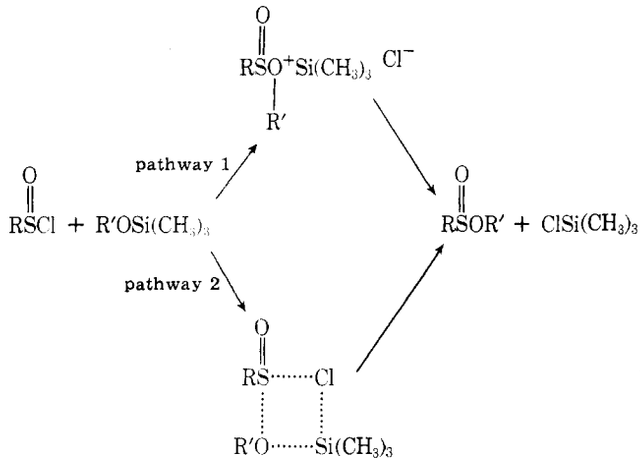
This result suggested that sulfenates could be conveniently converted to thiocyanates by reaction with trimethylsilyl cyanide.[18]

$$C_6H_5SOCH_3 + NCSi(CH_3)_3 \rightarrow C_6H_5SCN + CH_3OSi(CH_3)_3$$

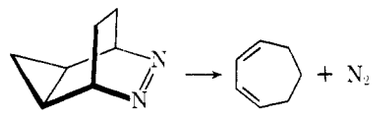
The reaction was essentially quantitative to form phenyl thiocyanate uncontaminated with the isothiocyanate.[19]

We felt that the mechanism of the exchange reaction was of considerable interest in that there appears to be a substantial number of synthetically useful silicon–halide interchange reactions of this general type (eq 1).[2b,h,4] Two distinct mechanistic pathways can be envisioned for the reaction of sulfinyl chlorides with trimethylsilyl ethers (Scheme I). In pathway 1, a charged intermediate is portrayed by attack of the ether oxygen on the electrophilic sulfinyl sulfur.[21] In the

Scheme I



second possibility, a four-center transition state is suggested which is associated with a minimum of charge generation.[24] A study of the effect of solvent polarity on reaction rate was helpful in differentiating these possibilities. If pathway 1 were operative, a rate increase of some several hundred would be expected in going from hydrocarbon solvents to methylene chloride,[26] while for the second, only a small change should be noted. A useful comparison in this regard obtains in the cheleotropic decomposition of **7.** This reaction has been



7

studied over a wide variety of solvent polarities from isooctane to 96% ethanol; a rate change of only 15-fold was noted.[27]

The rate of the silicon–halide interchange reaction was studied in five solvents (Table III) and a rate increase of only ninefold was found. This would be approximately the expected change if the transition state were nonionic.[28] In addition, such a transition state should be sensitive to steric factors. Consistent with this is the observation that when ethoxytrimethylsilane is used, an overall rate decrease of a factor of about 10 is observed, the same relative rates for each solvent being maintained.

We have found a number of formally analogous reactions between phosphorus and sulfur halides with trimethylsilyl derivatives of oxygen, nitrogen, and sulfur functions.[4e,29] These are under active investigation in our laboratory.

Experimental Section[30]

Preparation of the Silylated Alcohols. The required silylated alcohols were synthesized by essentially the same procedure. The alcohol (1.0 mol), hexamethyldisilazane (0.62 mol), and imidazole (0.5 g) were refluxed for 8 h. Distillation at reduced pressure (aspirator) removed the residual hexamethyldisilazane. Distillation of the residue under vacuum gave the product as a colorless oil. $(CH_3)_3SiOCH_3$: 53%; bp 57–58 °C (760 mm) [lit.[31] bp 67 °C (760 mm)]. $(CH_3)_3SiOC_2H_5$: 64%; bp 66–74 °C (760 mm) [lit.[32] bp 75 °C (760 mm)]. $(CH_3)_3SiOCH_2C_6H_5$: 88%; bp 82 °C (8.5 mm) [lit.[33] bp 92 °C (19 mm)]. $(CH_3)_3SiOC_{10}H_{19}$ (menthyl): 79%; bp 59–60 °C (0.35 mm).

Preparation of the Silylated Thiols. The procedure employed was as above.[34] $(CH_3)_3SiSCH_2C_5H_5$: 65%; bp 74–76 °C (0.6 mm); NMR (CCl_4) δ 0.3 [9 H, s, $Si(CH_3)_3$], 3.7 (2 H, s, CH_2), 7.2 (5 H, m, C_6H_5). $(CH_3)_3SiSC_6H_5$: 66%; bp 43–44 °C (1.1 mm) [lit.[34] bp 72–74 °C (3 mm)].

Preparation of Sulfinyl Chlorides. Methane and benzenesulfinyl chloride were prepared by the low temperature chlorination of the disulfide in the presence of acetic anhydride[35] in methylene chloride as solvent.[36] $CH_3(SO)Cl$: 70%; bp 46–48 °C (20 mm) [lit.[35] bp 47–48 °C (15 mm)]. $C_6H_5(SO)Cl$: 98%; n_D^{22} 1.6053 (lit.[35] n_D^{25} 1.6062).

α-Toluenesulfinyl chloride was prepared similarly by the chlorination of benzyl thiolacetate.[37] $C_6H_5CH_2(SO)Cl$: 90%; n_D^{22} 1.5784 (lit.[37] n_D^{25} 1.5872).

Table III.[a] Relative Rates of the Reaction $C_6H_5(SO)Cl + ROSi(CH_3)_3 \rightarrow C_6H_5(SO)OR + (CH_3)_3SiCl$

solvent	ε	10^5k, L mol^{-1} s^{-1} (R = C_2H_5)	k_{rel} (R = C_2H_5)	10^5k, L mol^{-1} s^{-1} (R = CH_3)
C_6D_{12}	2.02	3	1	
CCl_4	2.24	5	2	72
C_6H_6[b]	2.30	7	2	110
$CDCl_3$	4.81	16	5	150
CH_2Cl_2[b]	9.08	27	9	310

[a] The reaction was monitored by ^1H NMR spectroscopy (T = 36 ± 1 °C) using equal concentrations of substrate. [b] Added HCl increased the rate only by ~30%.

Benzyl Thiolacetate. Benzylthiotrimethylsilane (7.8 g, 0.04 mol) and acetyl chloride (4.7 g, 0.06 mol) were stirred together for 4 days. A small amount of solid material which had accumulated was collected and the volatiles were removed in vacuo. The resulting clear, colorless liquid was distilled under reduced pressure to give pure benzyl thiolacetate (6.1 g, 92%); bp 82–85 °C (1.75 mm) [lit.[38] 75–76 °C (0.8 mm)]; n_D^{24} 1.5581 (lit.[38] n_D^{25} 1.5565).

Sulfinate Esters. The procedure for the preparation of these materials was essentially the same for each member. Essential data are collected in Table I. Any deviations from the sample procedure (below) are cited.

Ethyl Methanesulfinate. Methanesulfinyl chloride (9.85 g, 0.10 mol) was introduced into a dry flask fitted with a pressure-equalizing dropping funnel. Ethoxytrimethylsilane (71.8 g, 0.10 mol) was placed in the dropping funnel and the apparatus was flushed with nitrogen. The ethoxytrimethylsilane was added dropwise over a period of 10 min, with constant stirring. The reaction appeared to be virtually complete overnight. Trimethylchlorosilane was removed by rotary evaporation and the resulting oil was distilled under reduced pressure: 8.7 g (81%); bp 85–87 °C (80 mm) [lit.[5a] 57–58 °C (25 mm)]; n_D 1.4357 (lit.[5a] n_D^{25} 1.4333).

Benzyl Benzenesulfinate. The reaction was carried out in the same way as for methyl methanesulfinate using benzenesulfinyl chloride (8.03 g, 0.05 mol) and benzyloxytrimethylsilane (9.0 g, 0.05 mol). Purification was achieved by column chromatography using Merck 7734 silica gel (70 g) and a column of diameter 2.5 cm. The eluant was a 30:70 percent mixture by volume of ethyl acetate and carbon tetrachloride. The appropriate fractions were concentrated by rotary evaporation and then subjected to a high vacuum (0.1 mm) for 1.5 h to remove last traces of solvent: yield 11.0 g (95%).

Benzyl α-Toluenesulfinate. α-Toluenesulfinyl chloride (5.82 g, 0.033 mol) was introduced into a round-bottom flask fitted with a pressure-equalizing dropping funnel. Benzyloxytrimethylsilane (6.00 g, 0.033 mol) was placed in the dropping funnel and the apparatus was flushed with nitrogen. The benzyloxytrimethylsilane was added over a period of about 10 min and the reaction mixture was stirred for 5 days; a white precipitate gradually formed. The reaction mixture was concentrated by rotary evaporation, several portions of carbon tetrachloride were added, and the mixture was evaporated again to ensure that trimethylchlorosilane was completely removed. The crystals were collected and washed with a small amount of diethyl ether. The crude material (4.0 g, 48%) was recrystallized from ethyl acetate: mp 49–50 °C (lit.[5e] mp 51–52 °C).

(−)-Methyl (−)-(*S*)-Benzenesulfinate. Benzenesulfinyl chloride (8.02 g, 0.05 mol) and *l*-menthoxytrimethylsilane (11.4 g, 0.05 mol) were mixed in a 50-mL round-bottom flask and the contents was stirred for 48 h. A very small amount of solid separated out and NMR showed the reaction to be about 95% completed. The reaction mixture was concentrated by rotary evaporation to remove trimethylchlorosilane; a slightly yellowish colored oil was obtained. This oil was taken up in methanol (40 mL) and the methanolic solution was cooled using dry ice. The resulting crystals were collected and washed with cold methanol. On standing the crystalline material changed to an oil–crystal mixture (6.35 g, 91%) which was then crystallized from methanol. This procedure was repeated and the crystals were washed using cold pentane: mp 37–40 °C (lit.[9b] 49–51 °C); $[\alpha]_D$ −195.3° (*c* 2.0, acetone) [lit.[9] $[\alpha]_D$ −205.5° (*c* 2.0, acetone)].

Unsymmetrical Disulfides. The procedure for the preparation of these compounds is the same for each one. Yields and properties are presented in Table II.

Benzyl *p*-Tolyl Disulfide. A solution of *p*-tolyl disulfide (6.16 g,

0.025 mol) in 50 mL of CCl_4, protected from moisture by a calcium chloride drying tube, was cooled to 0 °C, and sulfuryl chloride (3.38 g, 0.025 mol) was added followed by 3 drops of triethylamine. The red color of the sulfenyl chloride appeared immediately on mixing the reagents. The conversion was complete after 2 h by NMR analysis. This solution was then added dropwise to a solution of benzylthiotrimethylsilane (9.8 g, 0.05 mol) cooled in an ice–salt bath. The loss of color of the sulfenyl chloride was used as an end point for the reaction. The volatiles were removed by rotary evaporation, leaving a white solid which was crystallized from methanol to give 10.5 g (85%); mp 33–34 °C (lit.[12a] 34–35 °C).

Furfuryl Methyl Disulfide. Furfuryl mercaptan (1.14 g, 0.01 mol) was silylated in CCl_4 (25 mL) solution by treatment with 1-(trimethylsilyl)imidazole[39] (1.40 g, 0.01 mol). Imidazole was removed by filtration and the filtrate was treated dropwise with methanesulfenyl chloride[40] (0.94 g, 0.01 mol) in CCl_4 (25 mL) at 0 °C. After the addition was complete the volatiles were removed by rotary evaporation and the residue was distilled in vacuo to give 1.62 g (80%): bp 60–61 °C (0.8 mm); n_D^{23} 1.5661; $d^{22}{}_{22}$ 1.0796. The spectral properties (NMR, IR, MS) were identical with those in the literature.[14]

The Attempted Preparation of an Unsymmetrical Diaryl Disulfide. The reaction was carried out as above, using di-*p*-tolyl disulfide (3.08 g, 0.0125 mol), sulfuryl chloride (1.687 g, 0.0125 mol), and phenylthiotrimethylsilane (4.55 g, 0.025 mol). VPC analysis of the resulting reaction mixture indicated a 1:2:1 mixture of symmetrical/unsymmetrical/symmetrical disulfides, respectively.

Preparation of Furfuryl Methyl Disulfide from *N*-(Methylthio)succinimide. Furfuryl thiol (1.15 g, 0.01 mol) and *N*-(methylthio)succinimide (1.5 g, 0.01 mol) were refluxed in benzene (25 mL) for 72 h, after which time NMR showed the reaction to be complete. The reaction mixture was allowed to cool to room temperature and succinimide (0.88 g, 89%) was collected by filtration. After the filtrate was concentrated by rotary evaporation, the residue was distilled under reduced pressure to give 1.26 g (79%) of a colorless liquid, the properties of which were identical with those of the compound prepared by the sulfuryl chloride–alkylthiotrimethylsilane route.

Methyl Benzenesulfenate. A solution of diphenyldisulfide (21.8 g, 0.1 mol) in 200 mL of CCl_4, protected from moisture by a calcium chloride drying tube and cooled to 0 °C, was treated with sulfuryl chloride (13.5 g, 0.1 mol) followed by a few drops of triethylamine. The reaction mixture, which immediately turned red, was stirred for 2 h. The solvent was then removed by rotary evaporation, leaving benzenesulfenyl chloride as an oily, dark red liquid, which was used without further purification. The benzenesulfenyl chloride (28.8 g, 0.2 mol) was added dropwise to a solution of sodium methoxide [prepared from sodium (4.56 g, 0.2 mol) and methanol (200 mL)] cooled to −20°C. When the addition was completed, the solution was allowed to warm to room temperature. Methanol was removed by rotary evaporation and the residue was filtered of solid material. The filtrate was distilled under reduced pressure to give 2.8 g (10%): bp 49–51 °C (0.3 mm) [lit.[41] 88–89 °C (0.4 mm)].

Methyl *o*-Nitrobenzenesulfenate. A solution of sodium methoxide [prepared from sodium (0.46 g, 0.02 mol) and methanol (20 mL)] was added dropwise to a stirred solution of *o*-nitrophenylsulfenyl chloride (3.8 g, 0.02 mol) in 40 mL of methanol cooled in an ice bath. Addition was completed over a period of 20 min and stirring was then continued for a further hour. The reaction mixture was cooled to −20 °C and the resulting solid was collected by filtration. The product was recrystallized twice from methanol (1.24 g, 34%): mp 49–50 °C (lit.[42] 54 °C).

Reaction between Methyl *o*-Nitrobenzenesulfenate and Trimethylchlorosilane. Methyl *o*-nitrobenzenesulfenate (0.050 g, 0.27 mol) and trimethylchlorosilane (0.050 g, 0.43 mol) were introduced into an NMR tube containing deuterated chloroform (0.5 mL). NMR indicated that the reaction was >90% complete after 2 weeks and comparison of this spectrum with that of an authentic sample of *o*-nitrophenylsulfenyl chloride showed the two to be identical.

Reaction between Methyl Benzenesulfenate and Trimethylchlorosilane. Methyl benzenesulfenate (0.21 g, 1.9 mol) and trimethylchlorosilane (0.25 g, 2.2 mol) were mixed in an NMR tube. NMR indicated that the reaction was complete after 2 h. Comparison of the NMR spectrum with that of an authentic sample of benzenesulfenyl chloride shows that the features in the range δ 7.0–8.0 are identical.

Reaction between Methyl Benzenesulfenate and Trimethylsilyl Cyanide. Methyl benzenesulfenate (1.1 g, 7.9 mol) was dissolved in carbon tetrachloride (5 mL) and the solution was cooled to −20 °C using an acetone/dry ice bath. Trimethylsilyl cyanide (0.81 g, 7.9 mol) dissolved in carbon tetrachloride (5 mL) was added dropwise from a dropping funnel over a period of 10 min. The reaction mixture was allowed to warm to room temperature and the reaction was monitored by NMR. After 18 h the reaction was complete; carbon tetrachloride was removed by rotary evaporation. Vacuum distillation of the resulting residue gave a clear colorless liquid: bp 50–51 °C (1.0 mm) [lit.[43] 89–90 °C (8 mm)]; n_D^{26} 1.5704 (lit.[43] n_D^{25} 1.5712).

Reaction between *tert*-Butyl Hypochlorite and Benzylthiotrimethylsilane. Benzylthiotrimethylsilane (5.88 g, 0.03 mol) was dissolved in CCl_4 (25 mL) on a 50-mL round-bottom flask. *tert*-Butyl hypochlorite[44] (1.62 g, 0.015 mol) was added dropwise over 10 min; NMR showed the reaction was complete in 12 h. The *tert*-butoxytrimethylsilane was shown (NMR) to be present in the reaction mixture. The mixture was reduced in volume by rotary evaporation and the resulting dibenzyl disulfide recrystallized from ethanol (2.65 g, 62%): mp 68–71 °C; mmp 68–70 °C.

Reaction between *tert*-Butylhypochlorite and Phenylthiotrimethylsilane. The reaction was carried out as above. Diphenyl disulfide was formed (1.52 g, 47%): mp 60–61 °C; mmp 60–61 °C.

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Registry No.—$HOCH_3$, 67-56-1; HOC_2H_5, 64-17-5; $HOCH_2C_6H_5$, 100-51-6; $HOC_{10}H_{19}$, 2216-51-5; $(CH_3)_3SiOCH_3$, 1825-61-2; $(CH_3)_3SiOC_2H_5$, 1825-62-3; $(CH_3)_3SiOCH_2C_6H_5$, 14642-79-6; $(CH_3)_3SiOC_{10}H_{19}$, 66808-39-7; $CH_3(SO)Cl$, 676-85-7; $C_6H_5(SO)Cl$, 4972-29-6; $C_6H_5CH_2(SO)Cl$, 41719-05-5; C_6H_5SCN, 5285-87-0; hexamethyldisilazane, 999-97-3; acetyl chloride, 75-36-5; benzenethiolacetate, 32362-99-5; (−)-menthyl (*S*)-benzenesulfinate, 34513-32-1; *p*-tolyl disulfide, 103-19-5; furfuryl mercaptan, 98-02-2; *N*-(methylthio)succinimide, 63742-19-8; diphenyl disulfide, 882-33-7; benzenesulfenyl chloride, 931-59-9; methyl benzenesulfenate, 28715-70-0; methyl *o*-nitrobenzenesulfenate, 15666-75-8; *o*-nitrophenylsulfenyl chloride 7669-54-7; trimethylchlorosilane, 75-77-4; trimethylsilyl cyanide, 7677-24-9; dibenzyl disulfide, 150-60-7.

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Dinitromethane[1]

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Alkali salts of dinitromethane were obtained in high yields in the saponification of methyl cyanodinitroacetate or methyl dinitroacetate, prepared in the nitration of methyl cyanooximinoacetate and methyl malonate, respectively. These salts were used in the synthesis of fluorodinitromethane, fluorodinitroethanol, dinitroethanol, 2,2-dinitropropanediol, and dimethyl 4,4-dinitropimelate.

Potassium dinitromethane was first prepared by Villiers[2] in 1884 by reduction of bromodinitromethane, which was obtained[3] in low yields in the nitration of 2,4,6-tribromoaniline. Free dinitromethane,[4] an unstable pale yellow oil, decomposes readily at ambient temperatures. Dinitromethane was also obtained in low yields in the nitration of halogenated olefins, such as trichloroethylene.[5] More recently potassium dinitromethane was prepared[6] in 23% yield by the Ter Meer reaction[7] of chloronitromethane.

$$CH_3NO_2 + Cl_2 \rightarrow ClCH_2NO_2 \xrightarrow{KNO_2\text{-}KOH} K^+{}^-CH(NO_2)_2$$

Dinitromethane salts are also obtained from the alkali salts of dinitroethanol,[7] which are available in good yields in the oxidative nitration[8] of nitroethanol.

The present investigation resulted from a need for a more practical synthesis of dinitromethane salts. New routes to the compound were investigated based on methyl dinitroacetate and methyl cyanodinitroacetate.

The nitration of malonates was first investigated by Bouveault and Wahl[9] in 1903, who reported the synthesis of ethyl dinitroacetate with little experimental details. Kissinger and Ungnade[10] prepared a number of alkyl dinitroacetates in 10–20% yields in the nitration of alkyl malonates.

We obtained methyl malonate by a modification of a reported procedure;[11] yields were improved by 30% and the isolation procedure was simplified. The nitration of this monoester with nitrogen tetroxide, 100% nitric acid, nitric–sulfuric acid, and red fuming nitric acid was investigated. The best yield of methyl dinitroacetate, 55–60%, was obtained using an excess of 20% red fuming nitric acid in methylene chloride at 3–7 °C.

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