solution *N,N*-dichlorobenzenesulfonamide (**1a**; 6.8 g, 30 mmol) in dichloromethane (30 ml). Stirring is continued for 0.5 h at room temperature. The solvent is evaporated in vacuo and the residue distilled at reduced pressure to afford pure **5a**; yield: 5.5 g (70%); b.p. 94–95 °C/0.05 torr; n_D^{25}: 1.5250 (Ref.[9], b.p. 94–95 °C/0.05 torr; n_D^{25}: 1.5290).

N-Chloro-N-trimethylsilyl-4-toluenesulfonamide (5b):
Prepared as described from *N,N*-dichlorotoluenesulfonamide (**1b**); yield 63%; b.p. 104–105 °C/0.05 torr; n_D^{25}: 1.5300 (Ref.[9], b.p. 107–108 °C/0.06 torr; n_D^{25}: 1.5300).

Reaction of 4-Chlorobenzenesulfonamide with Chlorotrimethylsilane:
A mixture of the 4-chlorobenzenesulfonamide (19.2 g, 100 mmol), triethylamine (20.2 g, 200 mmol), and chlorotrimethylsilane (21.7 g, 200 mmol) in benzene (200 ml) is refluxed for 12 h. The precipitate is filtered off and the residue distilled in vacuo. According to ^{1}H-N.M.R. analysis, the resultant product (22.4 g, b.p. 124–135 °C/0.05 torr) is a mixture of *N*-trimethylsilyl-4-chlorobenzenesulfonamides. The individual products are isolated by fractional distillation to give: N,N-*bis[trimethylsilyl]-4-chlorobenzenesulfonamide* (**3c**); yield: 11.3 g (34%); b.p. 123–125 °C/0.05 torr [contaminated by 10–15% *N*-monosilylated product as determined by ^{1}H-N.M.R. analysis] and N-*trimethylsilyl-4-chlorobenzenesulfonamide*; yield: 10.2 g (39%); b.p. 130–135 °C/0.05 torr (Ref.[5], b.p. 128–129 °C/0.013 torr). This compound was identified by comparison of its I.R. and N.M.R. spectra with those of *N*-trimethylsilyl-4-chlorobenzenesulfonamide prepared according to Ref.[5].

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Phosphorus Pentasulfide and Thiophosphoryl Bromide: Facile Reagents for the Reduction of Sulfines to Thiones

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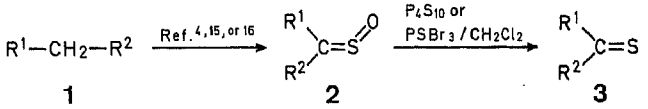
The class of compounds known as sulfines (thione *S*-oxides) has been known for many years and numerous compounds with this structural feature have been prepared, especially in the last few years[2,3]. In addition to the more familiar routes from sulfinyl chlorides by β-elimination and from thiones by oxidation, sulfines can now also be prepared in several cases from active methylene compounds via reaction of the corresponding silylated carbanions with sulfur dioxide[4]. Many reactions of sulfines have been investigated and it is thus remarkable that no synthetically useful procedure for the reduction of sulfines to thiones appears to have been reported so far, although some formation of thiones, accompanied by side-products, was found in the reaction of diaryl sulfines with metal carbonyls[5].

We were prompted by the successful application of phosphorus pentasulfide for the reduction of sulfoxides[6], as well as the related sulfimides[7] and selenoxides[6], to attempt to extend the range of this useful reagent to the sulfine (**2**) to thione (**3**) deoxygenation. This expectation has been fulfilled, as shown by the results in Table 1. The yields obtained are excellent, but the pattern of reaction times indicates some susceptibility to steric hindrance. As observed earlier for the sulfoxide deoxygenation[6], electron-releasing substituents appear to accelerate the reaction.

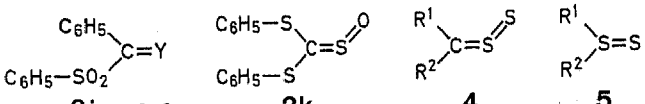


1 **2** **3**

Given the rather long reaction times required by some sulfines in the room temperature reaction with phosphorus pentasulfide, a number of reactions were also run for comparison in refluxing 1,2-dichloroethane and these results are reported in Table 2. Results obtained using the alternative reagent, thiophosphoryl bromide ($PSBr_3$)[8], are also reported in Table 2. The homogeneous reagent system of thiophosphoryl bromide in dichloromethane appears to be considerably more effective than the heterogeneous phosphorus pentasulfide reagent system under comparable conditions. Nevertheless, the phosphorus pentasulfide reagent allows somewhat easier product isolation, since this can be achieved without employing the aqueous (sodium hydrogen carbonate) work-up which is required when using thiophosphoryl bromide. Thus, for the more labile thione products, we see a definite advantage in the phosphorus pentasulfide method.

Our studies have shown that not all sulfines can be successfully reduced by the above procedures. For example, phenyl phenylsulfonyl sulfine (**2j**) appears to react slowly with both phosphorus pentasulfide and thiophosphoryl bromide but does not give the expected novel α-thioxosulfone **3j**, nor indeed any readily characterizable products. Both deoxygenating reagents surprisingly led to the formation of diphenyl disulfide in excellent yield on reaction with bis[phenylthio] sulfine (**2k**), rather than the expected diphenyl trithiocarbonate.

It appears that the deoxygenation reactions described herein may proceed through the intermediacy of the elusive thiosulfine species **4**[9], analogous to the thiosulfoxide species **5** proposed earlier as a short-lived intermediate in the sulfoxide deoxygenations[6,10]. Further work to elucidate the reaction mechanism is under way and will be the subject of a forthcoming publication.



2j Y = S=O
3j Y = S
2k **4** **5**

Since all of the sulfines **2** in Table 1 may be synthesized by the alkylidenation procedure[4], the new method described herein also constitutes the first known procedure for the conversion of appropriate methylene compounds **1** *directly* to the corresponding thiones **3**, *without* the intermediacy of the carbonyl analogues.

All of the sulfines **2** used in this study (with the exception of **2d**, see below) have been reported previously and were prepared either by oxidation of the corresponding thioxo compounds by published procedures[15,16] or by the alkylidenation route[4]. The commercially available

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Table 1. Reduction of Sulfines[a] **2** to Thiones **3** with Phosphorus Pentasulfide

Sulfine	R^1	R^2	Reaction time [h]	Yield [%][b]	m.p. [°C] found	m.p. [°C] reported
2a	C_6H_5	C_6H_5	6	58[c]	52–53°	51–53°[11]
2b	4-H_3C—C_6H_4	4-H_3C—C_6H_4	5.5	72[d]	76–77°	74–75°[11]
2c	4-H_3CO—C_6H_4	4-H_3CO—C_6H_4	2	83	120–121°	116–118°[11]
2d	4-$(H_3C)_2N$—C_6H_4	4-$(H_3C)_2N$—C_6H_4	1	95	210–211°	200–202°[11]
2e	2,4,6-tri-H_3C—C_6H_2	C_6H_5	48	94[e]	oil[f]	oil[12]
2f	C_6H_5	C_6H_5S	7	80	58–60°	59–60°[13]
2g	2,4,6-tri-H_3C—C_6H_2	C_6H_5S	20	92	92–93°	93–94°[13]
2h	2,4,6-tri-H_3C—C_6H_2	2,4,6-tri-H_3C—C_6H_2S	32	94	143–144°	142–143°[14]
2i	4-H_3C—C_6H_4	C_6H_5S	3.5	85	83–84°	83–84°[13]

[a] For unsymmetrically substituted sulfines, the (*Z*/*E*)-mixture of isomers was used. Procedure as exemplified by the reduction of **2c**.
[b] Yields represent isolated yields of thiones, the purity of which was also checked by I.R., ^{1}H-N.M.R., and T.L.C. (alumina) analysis.
[c] Chromatographed on Florisil with benzene; recrystallization from methanol (−20 °C under CO_2).
[d] Chromatographed on Florisil with benzene; recrystallized from dichloromethane/petroleum ether, 40–60 °C (−20 °C, under CO_2).
[e] After correcting for recovered starting material (30%).
[f] $C_{16}H_{16}S$ (240.4) calc. C 79.94 H 6.72 S 13.34; found 79.90 6.65 13.32

Table 2. Comparison of Alternative Procedures for Reduction of **2** to **3**

Sulfine	Procedure[a]	Time [h]	Yield [%]
2e	A	48	94[b]
	B	2	97
	C	4.5	90
2f	A	7	80
	B	1	95
	C	6	92
2g	A	20	92
	B	2	85
	C	3	95
2h	A	32	94
	B	2	95
	C	3.5	92

[a] Method A = P_4S_{10} (0.5 mol)/CH_2Cl_2/25 °C;
Method B = P_4S_{10} (0.5 mol)/$ClCH_2$—CH_2Cl/83 °C;
Method C = $PSBr_3$ (1.0 mol)/CH_2Cl_2/25 °C (details see procedure for **2h**).
[b] Reaction incomplete. The yield is corrected for recovered starting material (30%).

phosphorus pentasulfide (Fluka AG) and thiophosphoryl bromide (E. Merck, Darmstadt) were used as supplied. I.R. spectra were recorded on Perkin Elmer 257 or 298 spectrophotometers and ^{1}H-N.M.R. spectra on a Varian EM-390 instrument, operating at 90 MHz. Melting points are uncorrected. T.L.C. (to monitor the progress of the reactions) and column chromatography were conducted on alumina, with either benzene or diisopropyl ether/hexane mixture (1:2) as eluents. Microanalysis data were kindly obtained by Mr. A. F. Hamminga, Analytical Department, Rijksuniversiteit Groningen, 9747 AG Groningen, The Netherlands.

Bis[4-dimethylaminophenyl] Sulfine (2d):
This sulfine is obtained by oxidation of bis[4,4'-dimethylamino]thiobenzophenone in the usual way[15]. The sulfine; yield: 92%, is recrystallized as gold plates (chloroform/ether); m.p. 181–183 °C.

$C_{17}H_{20}N_2OS$ (330.3) calc. C 67.96 H 6.71 N 9.33 S 10.67; found 67.35 6.60 9.53 10.54

I.R. (KBr): $\nu_{C=S=O}$ = 1075, 1005, 985 cm^{-1}.

Reduction of Bis[4-methoxyphenyl] Sulfine (2c) with Phosphorus Pentasulfide:
To a stirred solution of the sulfine (0.50 g, 1.82 mmol) in dichloromethane (30 ml) is added phosphorus pentasulfide (0.41 g, 0.92 mmol). The reaction mixture is stirred for 2 h at 25 °C before filtering off the insoluble material. The precipitate is washed with dichloromethane (2 × 10 ml) and the combined dichloromethane solution washed thoroughly with 10% aqueous sodium hydrogen carbonate solution (3 × 20 ml) and then water (2 × 20 ml) before drying with magnesium sulfate. Removal of the solvent in vacuo and column chromatography on alumina, using benzene as eluent, gives a bright blue solid. Recrystallization from methanol at −20 °C gives blue crystals of 4,4'-dimethoxythiobenzophenone (**3c**); yield: 0.39 g (83%); m.p. 120–121 °C (Lit.[11], m.p. 116–118 °C).

Reduction of 2,4,6-Trimethylphenyl 2,4,6-Trimethylphenylthio Sulfine (2h) with Thiophosphoryl Bromide:
To a stirred solution of the sulfine (1.00 g, 3.03 mmol) in dichloromethane (50 ml), thiophosphoryl bromide (0.32 ml, 3.03 mmol) is added, using a syringe and septum cap. After stirring for 3.5 h at 25 °C, the mixture is washed thoroughly with 10% aqueous sodium hydrogen carbonate solution (3 × 20 ml), water (2 × 20 ml), and dried with magnesium sulfate. Removal of the solvent in vacuo and column chromatography on alumina, with benzene as eluent, gives an orange-red solid. Recrystallization from *n*-hexane affords 2,4,6-trimethylphenyl 2,4,6-trimethyldithiobenzoate (**3h**); yield: 0.88 g (92%); m.p. 143–144 °C (Lit.[14], m.p. 142–143 °C).

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A Novel Method for the α-Phenylthiomethylation of Carbonyl Compounds

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α-Phenyl- and α-alkylthiomethylations of carbonyl compounds are important synthetic reactions, since the thiomethylated products can also serve as precursors of α-methyl derivatives by reductive desulfurization with Raney nickel and as those of α-methylene derivatives by oxidative sulfur removal with sodium periodate. Recently, several groups[1-4] reported on the α-thiomethylation process; in general, using halomethyl sulfides, but the methods described are restricted and give poor yields of the products. The best method, the reaction of silyl enol ethers derived from ketones with phenyl chloromethyl sulfide in the presence of titanium(IV) chloride, was reported very recently[5].

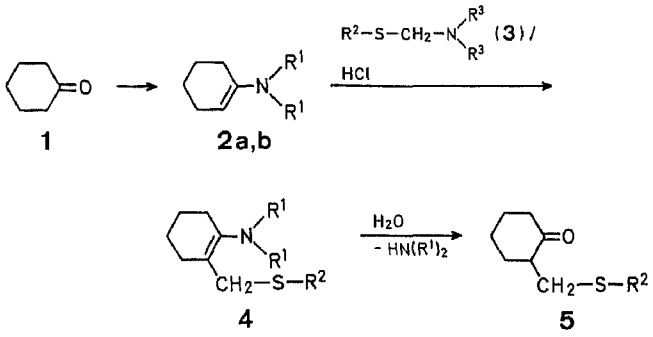
Acid-promoted phenyl- and alkylthiomethylation of aromatic compounds by the corresponding thiomethylamines has been reported[6]. We have investigated the possibility that the thiomethylation of enamines might offer a more convenient route to α-thiomethylated carbonyl compounds. We now report an effective method for α-thiomethylation of ketones and aldehydes, involving a thiomethylation of enamines, easily prepared from carbonyl compounds, by phenyl- and alkylthiomethylamines in the presence of hydrogen chloride, followed by hydrolysis of the mixture with hydrochloric acid.

Using *N*-cyclohexen-1-yl-dimethylamine (**2a**; $R^1 = CH_3$) and 4-cyclohexen-1-yl-morpholine [**2b**; $R^1—R^1 = —(CH_2)_2—O—(CH_2)_2—$], initial experiments were conducted by allowing them to react with the phenyl- or alkylthiomethylamine **3a-c** ($R^2 = C_6H_5$, $C_6H_5CH_2$, or CH_3) in the presence of hydrogen chloride in ethanol under reflux. Treatment of the concentrated residue with 20% hydrochloric acid gave the α-phenyl- and α-alkylthiomethylcyclohexanones (**5a-c**). Among these three thiomethylating reagents, the highest yield was obtained with the phenylthiomethylamine derivative **3a**.

Table 1. α-Phenylthiomethylation[a] of Cyclohexanone **1** to **5a** ($R^2 = C_6H_5$)

R^1 or R^1 R^1 in **2**	R^3 or R^3 R^3 in **3**	Reaction time [h]	Yield [%][b] of **5a**
$2CH_3$	$2CH_3$	2.0	63
$—(CH_2)_4—$	$2CH_3$	2.0	0
$—(CH_2)_5—$	$2CH_3$	1.5	73
$—(CH_2)_2—O—(CH_2)_2—$	$2CH_3$	1.0	80
$—(CH_2)_2—O—(CH_2)_2—$	$—(CH_2)_5—$	1.0	81
$—(CH_2)_2—O—(CH_2)_2—$	$—(CH_2)_2—O—(CH_2)_2—$	1.0	80

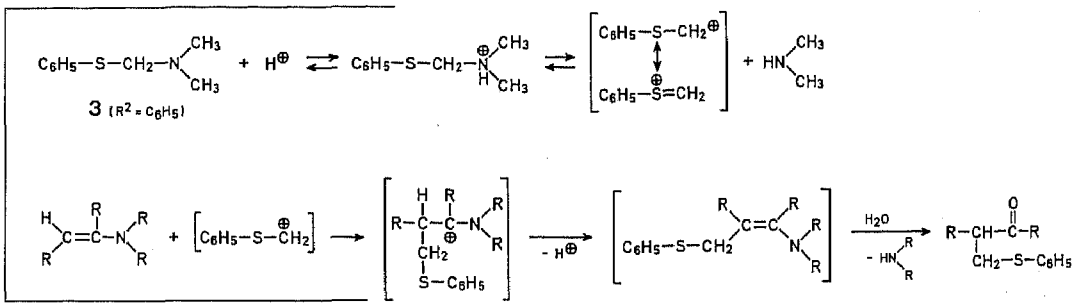
[a] Molar ratio of enamine **2**:**3**:HCl = 1:1:1.
[b] Yield of isolated product.



Control experiments included an examination of the efficiencies of the amine residues of the enamines prepared from cyclohexanone and those of the phenylthiomethylamines. As can be seen in Table 1, the yield of **5a** is greatly influenced by a change of the amine residue (R^1) of the enamines **2**; in the case of a pyrrolidine grouping [$R^1—R^1 = —(CH_2)_4—$], the reaction did not occur and the morpholine grouping [$R^1—R^1 = —(CH_2)_2—O—(CH_2)_2—$] is established as the most effective one. On the other hand, no appreciable difference in the yields was observed by a change of the amine residue (R^3) of the phenylthiomethylamines **3**.

Using **3a** ($R^2 = C_6H_5$, $R^3 = CH_3$) as a reagent, the phenylthiomethylation reaction was extensively examined with morpholine enamines, which were derived from cyclic and acyclic ketones and aldehydes. Results are summarized in Table 2. From the data in Table 2, it can be said that yield of the α-phenylthiomethylated product is lowered when the γ-carbon of enamine is branched (entries 1, 5, 9). Therefore, a higher yield is obtained in the case of an enamine possessing a β-methylene group (entries 7, 10). It is demonstrated by the use of 4-(2-methylpropene-1-yl)-morpholine that no reaction proceeds with enamines not possessing β-hydrogen atoms.

From the above facts, we suggest that the mechanism of this phenylthiomethylation reaction is as shown below. The reaction involves an electrophilic substitution of a phenylthiomethylcarbenium ion, derived



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