THIOSULFONIC S-ESTERS – 5[§]. MECHANISTIC ASPECTS OF THE REACTION WITH CHLOROTRIMETHYLSILANE AND SODIUM IODIDE

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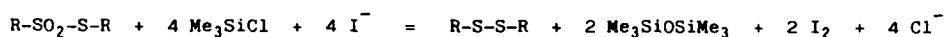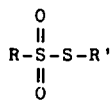Via Mezzocannone, 16   I-80134 Napoli (Italy)

Abstract: Thiosulfonic S-esters (1) are readily converted to disulfides (2) by chlorotrimethylsilane and sodium iodide. The reaction is shown to proceed through a complex mechanism, and more than one conversion pathway to disulfides must be considered. Evidence is presented for several S-S bond cleavage and reformation reactions involved in the conversion. In view of these results, the mechanistic interpretations proposed for already known reactions of various sulfur compounds with either chlorotrimethylsilane-iodide or iodotrimethylsilane should probably be revised. The behaviour of other reducing agents of thiosulfonates (1) to disulfides (2) was also checked.

In a previous paper we reported[1] that thiosulfonic S-esters (1), which are readily available[2] from sulfonyl chlorides, can be conveniently used to prepare disulfides. In fact, they are smoothly and quantitatively converted to the latter, by chlorotrimethylsilane and sodium iodide, in anhydrous acetonitrile at room temperature. The synthetic interest of this reaction was also shown to be restricted to the preparation of symmetrically substituted disulfides only: the unsymmetrically substituted thiosulfonic S-esters (1; R ≠ R'), under our experimental conditions, always afforded a mixture of three possible, one unsymmetrical and two symmetrical, disulfides. This aroused our interest to investigate the mechanistic course of the reduction, that apparently involves several sulfur-sulfur-bond cleavage and formation steps, rather than the simple multi-step reductive deoxygenation of the sulfonyl sulfur atom, as it could be expected in view of the current literature regarding reduction of sulfonic and sulfinic acid derivatives, accomplished by either chlorotrimethylsilane-sodium iodide itself[3] or related reagent systems.[4,5]

RESULTS

S-(4-methoxyphenyl) 4-methyl-benzenethiosulfonate (1b) was utilized as a model unsymmetrical thiosulfonic S-ester that, under our already mentioned reaction conditions[1] (see experimental), afforded three different disulfides,[6] namely 4-methylphenyl 4-methoxyphenyl disulfide (2b), bis(4-methoxyphenyl) disulfide (2c) and bis(4-methylphenyl) disulfide (2d). S-phenyl benzenethiosulfonate (1a) was instead utilized as a model symmetrical thiosulfonic S-ester. The determined stoichiometry of the overall reduction is:
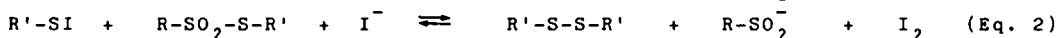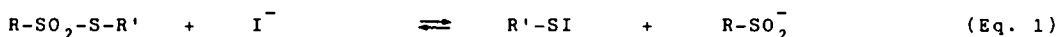
$$R\text{-}SO_2\text{-}S\text{-}R \; + \; 4\,Me_3SiCl \; + \; 4\,I^- \; = \; R\text{-}S\text{-}S\text{-}R \; + \; 2\,Me_3SiOSiMe_3 \; + \; 2\,I_2 \; + \; 4\,Cl^-$$

$$\begin{array}{cc}
\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{R-S-S-R'}}}} & R-S-S-R' \\
\\
1 & 2
\end{array}$$

a) R=R'=C$_6$H$_5$;   b) R=p-Me-C$_6$H$_4$, R'=p-MeO-C$_6$H$_4$;   c) R=R'=p-MeO-C$_6$H$_4$;   d) R=R'=p-Me-C$_6$H$_4$;
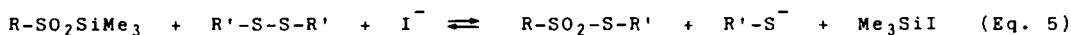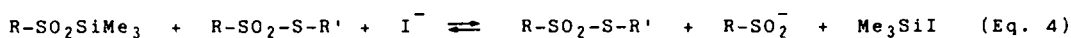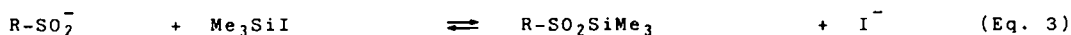
We started reasoning that the sulfonyl oxygen atoms in thiosulfonic S-esters are extremely weak bases[7,8] and, therefore, cannot afford any adducts with chlorotrimethylsilane (or its iodo-analog that can be formed in the reaction medium[9]). Thus, the iodide ion can be regarded as the sole (nucleophilic) reagent[10] initially active in the reaction mixture. It follows therefrom that the first step of the overall reaction may be confidently assumed to consist of the nucleophilic attack by the iodide ion at the sulfenyl sulfur atom of the starting thiosulfonate.[11-13] This would lead to the S-S bond cleavage and the formation of a sulfinate anion (likely silylated: vide infra) and a sulfenyl iodide (Cfr. Eq. 1). Due to the excess of iodide ions, and the consequent polarization of the S-I bond, the latter is a new sulfur nucleophile that can in its turn react with the starting thiosulfonate, affording disulfide, molecular iodine and a second sulfinate anion (Cfr. Eq. 2).

$$R-SO_2-S-R' \quad + \quad I^- \quad \rightleftharpoons \quad R'-SI \quad + \quad R-SO_2^- \qquad (Eq. 1)$$

$$R'-SI \quad + \quad R-SO_2-S-R' \quad + \quad I^- \quad \rightleftharpoons \quad R'-S-S-R' \quad + \quad R-SO_2^- \quad + \quad I_2 \qquad (Eq. 2)$$

In this view, S-phenyl benzenethiosulfonate (1a) was treated, under our experimental conditions (solvent, temperature, etc.), with sodium iodide only, i.e. with the exclusion of chlorotrimethylsilane. As expected, diphenyl disulfide (2a), sodium benzenesulfinate and molecular iodine were obtained in a 1:2:1 molar ratio, beside 10% of unreacted thiosulfonate 1a. In one of the experiments, a large excess (10:1 mol) of methyl iodide was added to the reagents. This led to the isolation of the expected methyl phenyl sulfone, resulting[14] from the reaction of methyl iodide with the sulfinate anion, accompanied (in a much smaller amount) by methyl phenyl sulfide, the formation of which is well accounted for by the occurrence of a sulfenyl iodide species in the reaction mixture. Accordingly, the unsymmetrically substituted thiosulfonate 1b, when treated with only sodium iodide under the same conditions, gave bis(4-methoxyphenyl) disulfide (2c) as the sole disulfide, beside sodium 4-methyl-benzenesulfinate.

These results clearly show that the nearly quantitative yield of disulfide(s), obtained when chlorotrimethylsilane is present in the reaction mixture, can only be accounted for by assuming that the sulfonyl moiety of the starting thiosulfonate, split off as sulfinate anion (Cfr. Eq. 1 and 2), is in turn involved in subsequent steps of the reduction. In fact, sodium arenesulfinates are reported[3] to react with chlorotrimethylsilane and sodium iodide, affording just disulfides. Therefore, we could confidently assume this reaction to represent the second step of the overall reduction. As a matter of fact, S-phenyl benzenethiosulfonate (1a) was treated with only sodium iodide, as described above, and three hours after the reaction was complete - i.e., when disulfide 2a, sodium benzenesulfinate, and unreacted starting thiosulfonate were in a quite definite molar ratio (see above) - chlorotrimethylsilane was added to the reaction mixture. (An aliquot was separated before chlorotrimethylsilane addition and put aside, as a comparison sample.) Within one hour, the precipitate, consisting of sodium benzenesulfinate, was completely solubilized and work up of the brown solution afforded disulfide 2a and starting thiosulfonate 1a, surprisingly in 62% and 35% yield (10% in the comparison sample).

In our opinion, the sharp increase of starting thiosulfonate, brought about by the addition of chlorotrimethylsilane to the reaction mixture, can be rationalized considering the reaction of chlorotrimethylsilane (and/or its iodo-analog[9]) with sodium sulfinate to afford a silyl sulfinate (Cfr. Eq. 3). The latter is soluble and can carry out a fast nucleophilic attack[15-17] onto either the unreacted thiosulfonate (ineffective, Cfr. Eq. 4) or the disulfide already formed, leading in this case to the formation of extra thiosulfonate.

$$R-SO_2^- \quad + \quad Me_3SiI \quad \rightleftharpoons \quad R-SO_2SiMe_3 \quad + \quad I^- \quad (Eq.\ 3)$$

$$R-SO_2SiMe_3 \ + \ R-SO_2-S-R' \ + \ I^- \rightleftharpoons \ R-SO_2-S-R' \ + \ R-SO_2^- \ + \ Me_3SiI \quad (Eq.\ 4)$$

$$R-SO_2SiMe_3 \ + \ R'-S-S-R' \ + \ I^- \rightleftharpoons \ R-SO_2-S-R' \ + \ R'-S^- \ + \ Me_3SiI \quad (Eq.\ 5)$$

However, it is evident that, in the case of the unsymmetrical thiosulfonate 1b, all the reactions so far considered cannot account for the formation of the unsymmetrical disulfide 2b as well as the symmetrical one, 2d, bearing two p-tolyl groups. Therefore, the key-step of the overall conversion is likely represented by the reduction of the silyl sulfinate 4 (Scheme) that can be accomplished by halotrimethylsilane species, leading to hexamethyldisiloxane and a new sulfenyl iodide 5. The latter can react, in its turn, with either the starting thiosulfonate 1b (at least in the early stages of the reaction) or the symmetrical disulfide 2c already formed, affording in both cases the unsymmetrical disulfide 2b, as shown in the Scheme. Evidence for the occurrence of 5 in the reaction mixture was achieved by carrying out the reduction of the unsymmetrical thiosulfonate 1b in the presence of a large excess of methyl iodide. In fact, under such conditions, 4-methylphenyl methyl sulfide could be detected among the reaction products, beside both the expected (Cfr. Eq. 1) 4-methoxyphenyl methyl sulfide and 4-methylphenyl methyl sulfone. (The latter is quite unaffected by the conditions used.) On the contrary, we could not detect any S-thiosulfinic esters (R-SO-S-R'; R = or ≠ R'), neither under our usual reaction conditions nor by using a rather low concentration of chlorotrimethylsilane and/or quenching the reaction at different stages before its completion. Indeed, S-thiosulfinic esters should result[18] from the reaction of a possible intermediate sulfinyl derivative R-SO-SiMe$_3$ with sulfenyl species like 3 or 5. Since specially prepared[19] samples of the above thiosulfinates, under our experimental conditions, did not undergo particularly fast reduction to the corresponding disulfides, we can assume that any possible intermediate sulfinyl species are rapidly deoxygenated[3] by halotrimethylsilane to sulfenyl iodide 5, too rapidly to be conveniently trapped by sulfenyl species.

In the Scheme we have outlined the various reactions so far determined, that appear to be involved in the conversion of an unsymmetrical thiosulfonate (namely, 1b) to disulfides. On the basis of our above results, the first step of the overall reaction is assumed to consist of iodide attack at the sulfenyl sulfur atom of the starting thiosulfonate with (concerted[7]) silylation of the leaving sulfinate anion to afford 3 and 4, both participating in subsequent reactions that have already been discussed. Several ways (may be more than those we tested) account for the formation of disulfides 2b and 2c, whereas no main way justifies the occurence of the symmetrical disulfide 2d. Actually, the latter could be formed by reaction of the sulfenyl iodide 5 with the unsymmetrical disulfide 2b, although, if one considers that both 2b and 2d appear in the reaction mixture almost at the same time, such a reaction is rather unlikely, at least in the early stages of the conversion, when the disulfide 2b is scarcely present at the equilibrium. By an independent way, the symmetrical disulfide 2d could be obtained from a new symmetrical thiosulfonate 1d, in turn deriving from 4, as shown in the Scheme. Indeed, 1d should afford the symmetrical disulfide 2d, either by direct reaction with the sulfenyl iodide 5 or through the reaction path(s) so far

SCHEME

$$\text{(1b)}\quad R\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}S\text{-}R' \;\overset{+SiMe_3}{\underset{-I}{}} \longrightarrow \quad R'\text{-}S\text{-}I \quad \xrightarrow[\;]{\;Me_3SiI\;(1b)\;} \quad R'\text{-}S\text{-}S\text{-}R' $$

3   2c

R-SO$_2$SiMe$_3$ 4

4 $\downarrow$ Me$_3$SiI → Me$_6$Si$_2$O

R-S-I   5

2b + 5 → (2c / 3, a; 1b / 4, b) → R-S-S-R'   2b

3 + 5 → R-S-S-R   2d

4 + (2b / 3, a; 5, b) → $R\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}S\text{-}R$ 1d → 2d

R=p-Me-C$_6$H$_4$; R'=p-MeO-C$_6$H$_4$;

discussed for its parent starting thiosulfonate 1b. Therefore, we checked the presence of such a new thiosulfonate in the reaction mixture and, working at rather low temperature,[20] could prove that 1d (isolated, and found identical with an authentic sample) is immediately formed, within the first few minutes of the reduction of 1b by chlorotrimethylsilane and sodium iodide. The occurrence of 1d in the early stages of the reaction confirms both that the reduction of the silylated sulfinate 4 is very fast (this is in agreement with the above mentioned unsuccessful attempts to trap possible intermediates of the reduction) and 4 itself is a good nucleophile[15] that attacks the sulfenyl iodide 5. The excess of iodide ion acts in the reaction mixture as a general base to accept Me$_3$Si$^+$ from the loosely[7] silylated thiosulfonate 1d. Considering the fast conversion 4 → 5, another possible way of formation of the thiosulfonate 1d, by rearrangement of its corresponding alpha-disulfoxide,[21,22] in turn resulting from the dimerization of intermediate sulfinyl species,[23] could be disregarded.

In view of the above results, we can conclude that the actual role played by chlorotrimethylsilane (and/or its iodo analog[9]) in the reduction of thiosulfonic S-esters (1) is the silylation of sulfinate anions leading to 4, and the subsequent (multi-step) deoxygenation of the latter, which splits off hexamethyldisiloxane to give the corresponding sulfenyl iodide 5. This role parallels with that of a protic acid. In fact, S-(4-methoxyphenyl) 4-methyl-benzenethiosulfonate 1b, when treated with hydriodic acid in acetone at room temperature, led in one hour to the same mixture of disulfides 2b, 2c and 2d in 82% overall yield. In this case, the protonation of the sulfinate anion yields sulfinic acid that is well known[24,25] to afford disulfides.

The results reported in this paper can be very useful to understand the course of already known reductions of various sulfur compounds, performed by halotrimethysilanes and related reagents. In

the light of our results, in fact, the mechanisms proposed for some of these reactions appear to be quite oversimplified and should probably be reconsidered.

EXPERIMENTAL

Thiosulfonic S-esters **1a**, **1c**, and **1d** were prepared according to a known procedure.[2] Chlorotrimethylsilane (Fluka, Switzerland) was purified[27] immediately before use. Anhydrous acetonitrile was obtained according to literature procedures.[28]

S-(4-methoxyphenyl) 4-methylbenzenethiosulfonate (1b).

To a magnetically stirred suspension of sodium 4-methylbenzenesulfinate (3.0 g; 16.8 mmol) in anhydrous ethanol (50 ml), solid S-(4-methoxyphenyl) 4-methoxybenzenethiosulfonate (**1d**) (1.0 g; 3.2 mmol) was added in one portion. After 6 hr at room temperature, the reaction mixture was diluted with water (30 ml) and extracted with Et$_2$O (2 x 100 ml). Evaporation in vacuo of the dried organic layer gave a crystalline crude residue that, after chromatographic separation (silica gel, hexane/Et$_2$O), afforded unreacted **1d** (0.2 g), and thiosulfonate **1b** (0.8 g), m.p. 53-55 °C, after crystallization from MeOH. (Found: C, 57.71; H, 4.60; S, 21.54; calc.d for C$_{14}$H$_{14}$O$_3$S$_2$: C, 57.12; H, 4.79; S, 21.78%.)

Reaction of S-(4-methoxyphenyl) 4-methylbenzenethiosulfonate (1b) with chlorotrimethylsilane and sodium iodide.

To a magnetically stirred solution of thiosulfonate **1b** (0.2 g; 0.7 mmol) in anhydrous MeCN (10 ml), cooled in a cold water bath and under dry nitrogen atmosphere, chlorotrimethylsilane (0.4 ml; 2.8 mmol) and dry sodium iodide (0.8 g; 5.6 mmol) were added in one portion. The clear solution became immediately red brown and the reaction was complete after 40' (TLC monitoring) and worked up in the usual way: addition of water (10 ml), extraction with Et$_2$O (3 x 10 ml), washing of the combined ethereal extracts with 5N aq sodium thiosulfate (20 ml) and finally with water. The evaporation of the dried organic layer in vacuo then gave a semicrystalline crude residue that, after chromatographic separation (silica gel, hexane), afforded three disulfides: bis(4-methylphenyl) disulfide **2d** (66 mg), m.p. 44-46 °C, after crystallization from hexane (lit.[29] 47-48 °C, from hexane)[30] bis(4-methoxyphenyl) disulfide **2c** (56 mg), m.p. 41-43 °C, after crystallization from hexane (lit. 44-45 °C, from MeOH), 4-methoxyphenyl 4-methylphenyl disulfide **2b** (38 mg), m.p. 44-45 °C, after crystallization from hexane. (Found: C, 63.76; H, 5.51; S, 24.72; calc.d for C$_{14}$H$_{14}$OS$_2$: C, 64.08; H, 5.38, S, 24.44%.)

Equilibration of disulfides 2b, 2c, and 2d.

A mixture of S-(4-methoxyphenyl) 4-methoxybenzenethiosulfonate **1c** (0.1 g; 0.3 mmol) and bis(4-methylphenyl) disulfide **2d** (30 mg, 0.1 mmol) was treated under the above conditions with chlorotrimethylsilane (0.2 ml; 1.3 mmol) and dry sodium iodide (0.4 g; 2.6 mmol). The chromatographic separation (silica gel, hexane) of the crude reaction product afforded three disulfides: **2d** (16 mg), m.p. 46-47 °C (from hexane), **2c** (70 mg), m.p. 40-42 °C (from MeOH), and **2b** (10 mg), m.p. 46-47 °C (from hexane).
Under the same conditions, a sample of unsymmetrical disulfide **2b** (0.2 g; 0.8 mmol) gave, after 1 hr, a mixture containing **2c** (18 mg) and **2d** (26 mg).

Reactions of thiosulfonic S-esters 1a and 1b with sodium iodide in anhydrous acetonitrile.

To a magnetically stirred solution of dry sodium iodide (4.8 g; 32.0 mmol) in anhydrous MeCN (30 ml), under dry nitrogen atmosphere, S-phenyl benzenethiosulfonate (**1a**) (1.0 g; 4.0 mmol), dissolved in few ml of the same solvent, was added in one portion. The clear solution became red brown and a white crystalline solid (sodium benzenesulfinate) began to precipitate. GLC monitoring of the MeCN solution showed presence of starting thiosulfonate **1a** and diphenyl disulfide **2a** in a ratio that remained unchanged after 30'. The reaction mixture was then filtered and sodium benzenesulfinate rapidly washed with anhydrous MeCN, and dried over phosphorus pentoxide. (Three runs: average yield 0.6 g; 3.4 mmol; m.p. > 300 °C, dec.; IR, nuyol: 1020, 970 cm^{-1}; Found: C, 44.30; H, 2.95; calc.d for C$_6$H$_5$O$_2$SNa: C, 43.90; H, 3.07%.) The MeCN solution was diluted with 5N aq sodium thiosulfate (20 ml) and extracted with Et$_2$O (3 x 30 ml). The combined organic layers, washed with water, dried, and evaporated in vacuo, gave a crude semicrystalline residue whose chromatographic separation (silica gel, hexane) afforded[30] diphenyl disulfide **2a** (0.4 g; 1.8 mmol), m.p. 58-60 °C, after crystallization from MeOH (lit. 59-60 °C, from EtOH), and unreacted starting thiosulfonate **1a** (0.1 g; 0.4 mmol; 10%).
In one experiment, iodine was titrated by N sodium thiosulfate (1.8 meq consumed).
Under the same conditions, S-(4-methoxyphenyl) 4-methylbenzenethiosulfonate (**1b**) (1.0 g; 3.4 mmol)

afforded sodium 4-methylbenzenesulfinate (0.6 g; 3.1 mmol), m.p. > 290 °C, dec. (IR, nuyol: 1027, 965 cm^{-1}), beside bis(4-methoxyphenyl) disulfide 2c (0.4 g; 1.6 mmol), m.p. 42-44 °C, from hexane. Unreacted starting thiosulfonate was also recovered, in a small amount (60 mg; 0.2 mmol; 6%).

Reactions of thiosulfonic S-esters 1a and 1b with sodium iodide and excess methyl iodide.

To a solution of dry sodium iodide (4.9 g; 32.8 mmol) in anhydrous MeCN (60 ml), under the conditions reported above, methyl iodide (2.5 ml; 40.0 mmol) and S-phenyl benzenethiosulfonate (1a) (1.0 g; 4.0 mmol), dissolved in few ml of the same solvent, were added, both in one portion. After 1 hr, the usual work up of the reaction mixture, as described above, gave a crude residue[31] whose chromatographic separation (silica gel, hexane/Et$_2$O) afforded: oily methyl phenyl sulfide (10 mg), ^{1}H NMR (CCl$_4$): δ 2.35 (s, 3H, CH$_3$-S-); diphenyl disulfide (2a) (0.4 g), m.p. 58-60 °C, from hexane; unreacted starting thiosulfonate (1a)[32] (30 mg; 3%); methyl phenyl sulfone (84 mg), m.p. 85-86 °C from MeOH (lit.[32] 88 °C, from H$_2$O), ^{1}H NMR (CCl$_4$): δ 2.90 (s, 3H, CH$_3$-SO$_2$-).
Under the same conditions, S-(4-methoxyphenyl) 4-methylbenzenethiosulfonate (1b) (1.0 g; 3.4 mmol) afforded: 4-methoxyphenyl methyl sulfide (15 mg), b.p. 200-210 °C (lit.[1] 211-212 °C); bis(4-methoxyphenyl) disulfide (2c) (0.5 g), m.p. 41-43 °C, from hexane; unreacted starting thiosulfonate (1b)[32] (25 mg; 2.5%); 4-methylphenyl methyl sulfone (0.1 g), m.p. 86-87 °C, from benzene/hexane (lit.[1] 89 °C, from hexane).

Reaction of S-phenyl benzenethiosulfonate (1a) and sodium iodide with delayed addition of chlorotrimethylsilane.

The reaction of 1a (1.0 g; 4.0 mmol) with dry sodium iodide (4.9 g; 32.8 mmol) in anhydrous MeCN (60 ml) was carried out as described above. It was complete after 30' and GLC monitoring of the MeCN solution was pursued for 3 hr to ascertain the presence of diphenyl disulfide (2a) and the unreacted starting thiosulfonate 1a in a constant ratio (82:18). A chromatographic sample of the solution was then separated and kept as a reference sample. To the remaining reaction mixture, chlorotrimethylsilane (2.1 ml; 16.4 mmol) was added in one portion, under the same conditions. The crystalline precipitate slowly disappeared and, after 1 hr, was completely solubilized. The usual work up of the clear red brown reaction mixture, followed by chromatography (silica gel, hexane) of the crude product afforded diphenyl disulfide (2a), m.p. 58-60 °C, from MeOH (0.5 g; 2.5 mmol; yield 62%) and starting thiosulfonate 1a (0.35 g; 1.4 mmol, yield 35%). The yield of 1a in the reference sample was 10%.

Reaction of thiosulfonic S-ester 1b with chlorotrimethylsilane, sodium iodide, and excess methyl iodide.

To a magnetically stirred solution of thiosulfonate 1b (1.0 g; 3.4 mmol) in anhydrous MeCN (40 ml), under the conditions described above, chlorotrimethylsilane (1.8 ml; 14 mmol), sodium iodide (4.2 g; 28 mmol), and methyl iodide (2.2 ml; 35.0 mmol) were added in sequence. Usual work up of the reaction mixture after 1 hr and chromatography (silica gel, hexane/Et$_2$O)[32] of the resulting crude residue afforded: oily 4-methylphenyl methyl sulfide (15 mg); bis(4-methylphenyl) disulfide (2d) (0.3 g), m.p. 44-46 °C (from hexane); bis(4-methoxyphenyl) disulfide (2c) (0.3 g), m.p. 41-43 °C (from hexane); 4-methoxyphenyl 4-methylphenyl disulfide (2b) (0.2 g), m.p. 44-45 °C (from hexane); 4-methylphenyl methyl sulfone (60 mg), m.p. 87-88 °C, from EtOH.

Treatment of 4-methylphenyl methyl sulfone with chlorotrimethylsilane and sodium iodide.

A solution of pure 4-methylphenyl methyl sulfone (0.5 g; 2.9 mmol), chlorotrimethylsilane (0.7 ml; 5.8 mmol), and sodium iodide (1.7 g; 11.6 mmol), in anhydrous MeCN (40 ml), was stirred for 3 hr under the conditions described above. Usual work up of the reaction mixture yielded unchanged starting material (0.5 g) free of any traces of the corresponding 4-methylphenyl methyl sulfide.

Reaction of S-phenyl benzenethiosulfinate with chlorotrimethylsilane and sodium iodide.

To a magnetically stirred solution of the title S-thiosulfinic ester[19] (0.5 g; 2.1 mmol), in anhydrous MeCN (30 ml), cooled in a cold water bath and under dry nitrogen atmosphere, chlorotrimethylsilane (0.5 ml; 4.3 mmol) and dry sodium iodide (1.3 g; 8.5 mmol) were added in one portion. The clear solution became immediately red brown, and the reaction, monitored by TLC, was complete within 50'. Work up as usual and chromatography (silica gel, hexane) of the crude reaction product afforded practically pure diphenyl disulfide (2a) (0.47 g), m.p. 58-60 °C (from hexane).

S-(4-methylphenyl) 4-methylbenzenethiosulfonate from the reaction of 1b with chlorotrimethylsilane and sodium iodide.

The reaction of the unsymmetrical thiosulfonate 1b (2.0 g; 6.8 mmol) with chlorotrimethylsilane (3.5 ml; 28.0 mmol) and sodium iodide (8.4 g; 56.0 mmol) in anhydrous MeCN (120 ml) was carried out under the conditions reported above but the temperature, since the initial thiosulfonate solution was cooled in a carbon dioxide/acetone bath. After the addition of chlorotrimethylsilane and sodium iodide, the clear solution remained colorless and GLC monitoring showed the reaction not to start at all, under such conditions. The temperature was let to arise slowly and the reaction started sluggishly in the range -20 + -10 °C. GLC monitoring was pursued at 5' intervals and, after 20', the concentration of the symmetrical thiosulfonate 1d (by comparison with a specially prepared sample) appeared to be convenient for isolation. The reaction was then quenched by addition of water (60 ml) and worked up as usual. Chromatographic separation of the crude product (silica gel,

hexane) afforded the unreacted starting thiosulfonate **1b**, as the main product (1.8 g), besides a a mixture of disulfides **2b, 2c, 2d**, and symmetrical thiosulfonate **1d** (25 mg), m.p. 73-75 °C, from hexane (mixed m.p. 71-74 °C, with a specially prepared sample).

Reaction of S-(4-methoxyphenyl) 4-methylbenzenethiosulfonate (1b) with hydriodic acid.

To a magnetically stirred solution of the title thiosulfonate **1b** (0.5 g, 1.7 mmol) in acetone (30 ml), 57% w/w aq hydriodic acid (1.1 ml; 14.6 mmol) was added and the reaction mixture was left at room temperature for 1 hr, under hydrogen atmosphere. Work up of the reaction mixture as usual and chromatographic purification (silica gel, hexane) of the crude reaction product afforded disulfides **2b, 2c,** and **2d** in 82% overall yield (0.43 g; 1.4 mmol: average MW = 262).

REFERENCES AND NOTES

§ For Part 3 and 4 in the same series, see Ref. 13 and 26.

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