Silicon in Organosulfur Chemistry. Part 3.[1] Disulfide–Silyl Sulfide Interchange. A New Aspect of the Thiol–Disulfide Interchange

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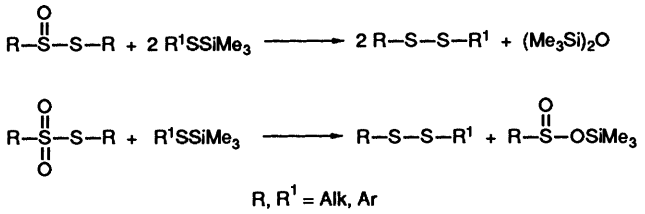
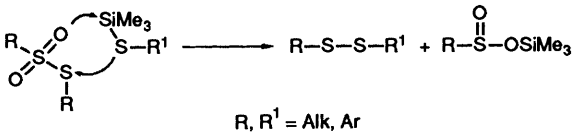
Aryl silyl sulfides (**2**) undergo interchange reactions with disulfides while, under the same reaction conditions, the corresponding alkyl silyl sulfides are unreactive. Furthermore, the reaction of alkyl aryl disulfides with arylthiosilanes shows a peculiar selectivity in that exchange of the arylthio residues only is observed. This reaction, which represents a new aspect of the well known thiol–disulfide interchange, takes place under mild and neutral conditions. A possible rationalization of the mechanism of this new reaction is also proposed.

A few years ago we reported the reaction of thiolsulfonates and thiosulfinates with trimethylsilyl sulfides which, in chloroform at 60 °C, gave disulfides[1] (Scheme 1). In particular the reaction



Scheme 1

of dialkyl thiolsulfonates with alkyl or aryl silyl sulfides gave good yields of unsymmetrical alkyl aryl disulfides. For this reaction we proposed the mechanism reported in Scheme 2.



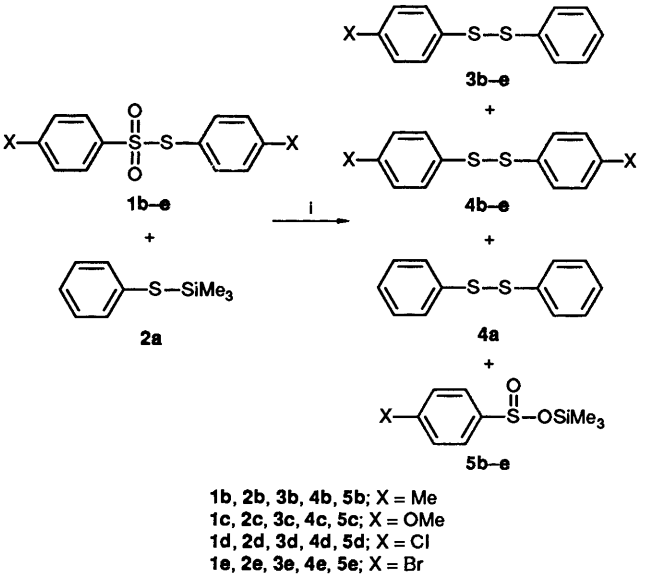
Scheme 2

Results and Discussion

Reaction of Thiolsulfonates **1** *with Phenylthiotrimethylsilane* **2a**.—Following our studies on the reactivity of thiolsulfonates with silyl sulfides we tried to take advantage of this reaction to synthesize unsymmetrical diaryl disulfides. In fact it is well known that these species easily undergo exchange of the aryl residues to give mixtures of unsymmetrical and symmetrical disulfides.[2]

The reaction of thiolsulfonates **1b–e** with phenylthiotrimethylsilane **2a**, in $CDCl_3$ at 60 °C, gave the expected unsymmetrical disulfides **3b–e**. However they were contaminated by variable amounts of the symmetrical disulfides **4** (Scheme 3). ^{13}C NMR spectroscopy turned out to be a useful tool for qualitative and quantitative analysis of the reaction mixture.[3] The integral ratio of signals of corresponding carbon atoms in different disulfides was used for quantitative analysis. It is reasonable to assume similar relaxation times for so related carbon atoms. In particular we utilized the ^{13}C chemical shifts of the sulfur-bonded aromatic carbon atoms of **3** and **4** which were different enough to allow correct calculation of their ratio. Yields and ratios of the different disulfides obtained in the reactions of **1b–e** with **2a** are reported in Table 1.

The formation of symmetrical disulfides **4** cannot be accounted for by the general mechanism shown in Scheme 2.



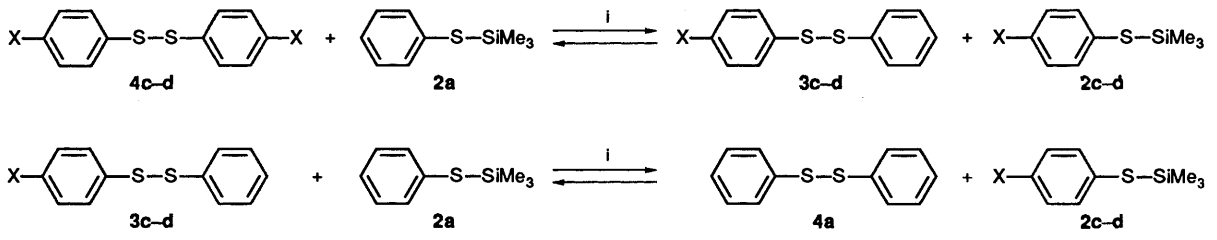
Scheme 3 *Conditions:* i, $CDCl_3$, 60 °C

The formation of these species might be due to several side reactions occurring in our system: (i) hydrolysis of **2a** to give benzenethiol that should be able to promote the exchange of the aryl residues of the disulfides;[4] (ii) thermal decomposition of the thiolsulfonates **1** which might initiate a radical process; (iii) thermally induced exchange of the unsymmetrical disulfides.[5]

We checked carefully by ^1H NMR spectroscopy the absence of any hexamethyldisiloxane, which is a good tracer for hydrolytic processes of silylated species. Furthermore, we demonstrated, by ^1H and ^{13}C NMR spectroscopy, the stability of thiolsulfonates **1b–e** under the reaction conditions.

The thermal stability of the disulfides was checked by heating at 60 °C in $CDCl_3$ equimolar amounts of **4a** and **4d**. In this case ^{13}C NMR spectroscopy did not show formation of any unsymmetrical species. However 5% of 4-bromophenyl phenyl disulfide **3e** was observed upon heating at 60 °C for 24 h a mixture of diphenyl disulfide **4a** and bis(4-bromophenyl) disulfide **4e**. These results indicate that, although under our reaction conditions thermal exchange can to some extent be operative, other mechanisms must also be involved to explain the large randomization of the arylthio residues observed.

Phenylthiotrimethylsilane–Diaryl Disulfides Interchange.—A possible explanation for the formation of unsymmetrical disul-



Scheme 4 *Conditions:* i, $CDCl_3$, 60 °C

Table 1 Yields of unsymmetrical and symmetrical disulfides (%) obtained in the reaction of thiolsulfonates **1** with phenylthiotrimethylsilane **2a** in $CDCl_3$ at 60 °C[a]

X	Product			Reaction time/h	Isolated[b] yields (%)
	X—⟨⟩—S—S—⟨⟩	X—⟨⟩—S—S—⟨⟩—X	⟨⟩—S—S—⟨⟩		
Me[c]	59 (62)	26 (29)	15 (10)	22	93
OMe	64 (55[d])	18 (21[d])	18 (23[d])	25	99
Cl	74 (77)	20 (16)	6 (6)	18	86
Br	63 (65)	19 (15)	18 (20)	42	91

[a] Data refer to percentages calculated by integration of ^{13}C NMR signals of quaternary carbons α to sulfur in the crude reaction mixtures. Data in parentheses refer to mixtures of disulfides after preparative TLC. [b] Yields refer to the mixture of disulfides. [c] A different result was found using slightly different conditions.[3] [d] Data refers to disulfides separated after preparative TLC.

Table 2 ^{13}C NMR-measured percentages of the species present in the reaction mixture of **2a** with **4c** or **4d** after 27 h at 60 °C in $CDCl_3$

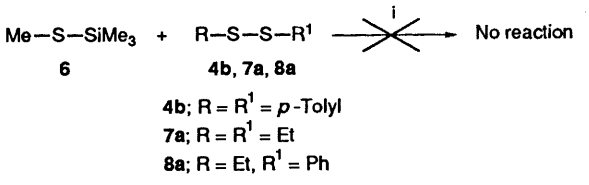
	X = OMe	X = Cl
X—⟨⟩—S—S—⟨⟩—X	42	28
⟨⟩—S—SiMe3	32	21
X—⟨⟩—S—S—⟨⟩	12	23
X—⟨⟩—S—SiMe3	11	23
⟨⟩—S—S—⟨⟩	3	5

fides in reactions described in Scheme 3 might be an exchange between the disulfides **3** and the silyl sulfide **2a** (Scheme 4). In order to verify this hypothesis we reacted equimolar amounts of **4c** or **4d** with **2a** at 60 °C in $CDCl_3$. In both cases we detected by ^{13}C NMR spectroscopy the formation of new disulfides and arylthiosilanes (Scheme 4). All the species present in solution were identified by comparison with the ^{13}C NMR spectra of authentic samples. Relevant data of the reaction mixtures, obtained without any manipulations, are shown in Table 2.

* Attempts to reach the same equilibrium mixture from the reaction of **4c** and **2a**, and from that of **4a** and **2c**, failed because after 300 h at 60 °C some hydrolysis of thiosilanes was observed without the reaction had reached the equilibrium.

The data presented here clearly show that diaryl disulfides and phenylthiotrimethylsilane undergo an exchange reaction under conditions similar to those employed for the reaction of thiolsulfonates with **2a**.* Therefore it is reasonable to assume that the formation of symmetrical disulfides in the reaction of **2a** and **1** (Scheme 3) arises from the exchange between unsymmetrical diaryl disulfides formed in the reaction mixture and phenylthiotrimethyl silane **2a**. This new exchange reaction prompted us to investigate in more detail the influence of the nature of the disulfides and thiosilanes.

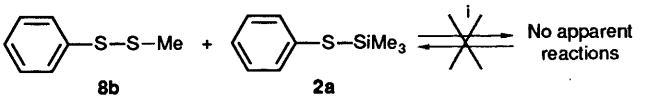
Methylthiotrimethylsilane–Disulfides Reaction.—We checked the ability of methylthiotrimethylsilane **6** to exchange the methylthio residue with different classes of disulfides. The reaction of **6** in $CDCl_3$ at 60 °C with di-*p*-tolyl disulfide **4b**, diethyl disulfide **7a** and phenyl ethyl disulfide **8a** did not show any exchange of the methylthio residues (Scheme 5). Thus in our



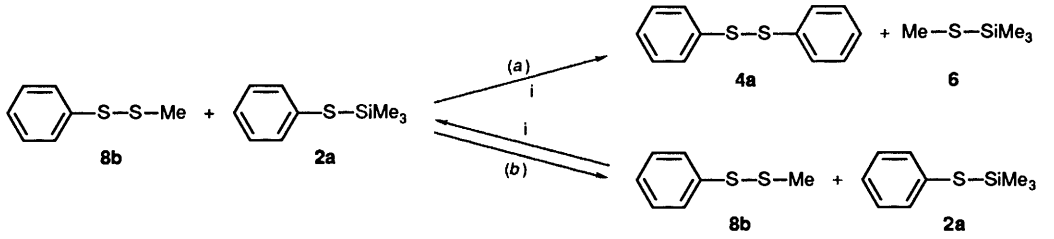
Scheme 5 *Conditions:* i, $CDCl_3$, 60 °C

reaction conditions methylthiotrimethylsilane **6** behaves differently from the phenylthiosilane **2a**.

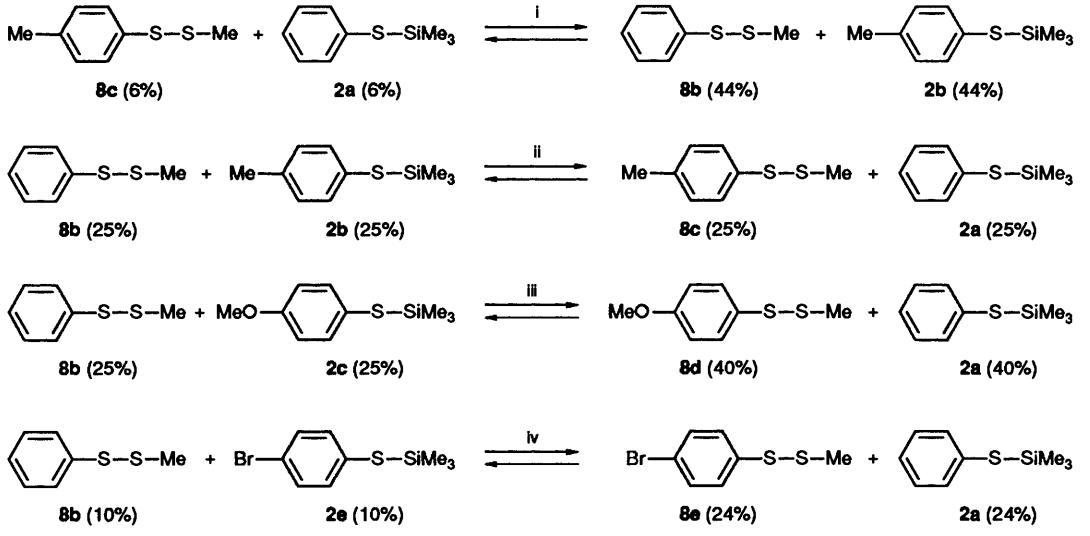
Arylthiotrimethylsilanes **2***–Alkyl Aryl Disulfides* **8** *Interchange.*—The next case we considered was the reaction of phenylthiosilane **2a** with phenyl methyl disulfide **8b**. We did not observe any exchange reaction even after 40 h at 60 °C in $CDCl_3$ (Scheme 6). This result is quite unexpected since phenyl-



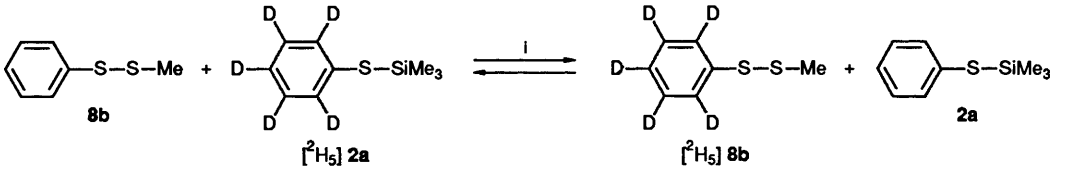
Scheme 6 *Conditions:* i, $CDCl_3$, 60 °C



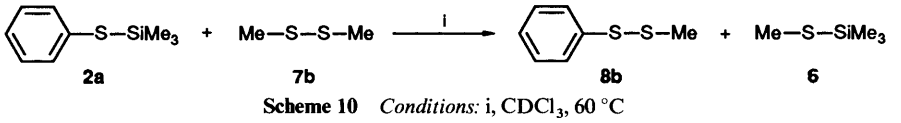
Scheme 7 *Conditions:* i, $CDCl_3$, 60 °C



Scheme 8 *Conditions:* $CDCl_3$, 60 °C; i, After 110 h; ii, After 100 h; iii, After 120 h; iv, After 115 h



Scheme 9 *Conditions:* i, $CDCl_3$, 60 °C



Scheme 10 *Conditions:* i, $CDCl_3$, 60 °C

thiotrimethylsilane **2a** reacts with diaryl disulfides **4**. However the interaction between **2a** and phenyl methyl disulfide **8b** can in principle occur in two ways (Scheme 7).

The attack of **2a** at the sulfur linked to the phenyl group of **8b** [path (*a*)] should be irreversible since it generates an alkylthiosilane which is unreactive in this system (see Scheme 5). On the other hand the attack at the sulfur bonded to the methyl group regenerates the same species [path (*b*)]. Thus our result might be explained by assuming path (*b*) only to be operating.

This selectivity has been proved by a number of reactions: we reacted phenylthiotrimethylsilane **2a** with *p*-tolyl methyl disulfide **8c** and the silanes **2b**, **2c** and **2e** with phenyl methyl disulfide **8b** (Scheme 8). In all reactions we observed, by ^1H NMR spectroscopy, the formation of the new aryl methyl disulfide, while we never detected the presence of methylthiosilane or that of the mixed diaryl disulfides which could be formed according to path (*a*) of Scheme 7. Therefore we reconsidered the reaction of phenylthiotrimethylsilane with phenyl methyl disulfide **8b** (Scheme 6). In order to demonstrate further the selectivity of the reaction we synthesized [$^2H_5$]-phenylthiotrimethylsilane which was then reacted with **8b** (Scheme 9). The reaction was monitored by means of GC–MS SIM methodology which showed that 14% of exchange had occurred after 42 h at 60 °C. These data reveal a peculiar selectivity of the interchange between aryl silyl sulfides and alkyl aryl disulfides.

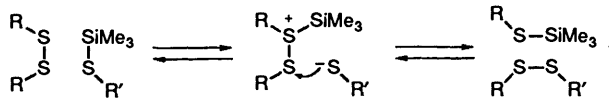
Phenylthiotrimethylsilane–Dimethyl Disulfide Interchange.—The reaction of phenylthiotrimethylsilane with dimethyl disulfide **7b** under the same reaction conditions ($CDCl_3$, 60 °C) gave exchange of the methylthio residue affording phenyl methyl disulfide **8b** and thiosilane **6** (Scheme 10).

In this case it was possible to follow the reaction by monitoring the ^1H NMR signals of the different methyl residues of **6**, **7b** and **8b**, while no indications of the formation of diphenyl disulfide were detected by means of ^{13}C NMR spectroscopy or GC–MS techniques. ^1H NMR analysis of the mixture even after 250 h at 60 °C showed the presence of reagents and products in 1:1 ratio (see Experimental Section). As we have shown (Scheme 5) methylthiotrimethylsilane **6** does not react with disulfides so that the reaction between **2a** and **7b** cannot be considered an equilibrium. However the unproductive exchange of phenylthio residues between silane **2a** and disulfide **8b**

(Scheme 7) does not allow a complete shift to the right of the reaction described in Scheme 10.

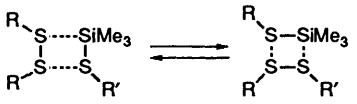
Conclusions

Ionic or concerted mechanisms can be drawn to describe this new exchange reaction. Taking into account the structure of the reagents an ionic mechanism would assume the silylation of the disulfide by the silyl sulfide followed by a nucleophilic attack of the thiolate ion on the silylsulfonium salt formed (Scheme 11).



Scheme 11

On the other hand the reaction conditions might also suggest a four-centre mechanism (Scheme 12). A similar mechanism has been postulated for the electrophilic activation in nucleophilic substitution at disulfide sulfur.[6]



Scheme 12

Our data cannot distinguish between them however two points deserve some comment: firstly the lack of reactivity of alkylthiosilanes towards disulfides, and secondly the selectivity observed in the reaction between aryl alkyl disulfides and arylthiosilanes. The former might be linked to different d_π–d_π interaction between silicon and alkylthio or arylthio residues: a weaker bond, which makes the exchange feasible, is expected for arylthio silanes. The latter might be explained by the more pronounced leaving group ability of arylthio residues with respect to the alkylthio groups, the influence of the thiol pK_a in the thiol–disulfide interchange has been well documented:[7] in this type of reaction the more acidic thiol is usually the better leaving group. These data are in agreement with the selectivity observed in the reaction of arylthiosilanes with alkyl aryl disulfides independently of the real operative mechanism.

In conclusion we have shown that dialkyl or diaryl disulfides undergo interchange of a thioresidue with arylthiosilanes but not with alkylthiosilanes, indicating a peculiar selectivity. Moreover arylthiosilanes show an even more unexpected selectivity in the interchange reaction with aryl alkyl disulfides. The data presented in this paper also indicate that the reaction of arylthiolsulfonates with arylthiosilanes cannot be utilized for the selective synthesis of unsymmetrical disulfides because of the silyl sulfide–disulfide interchange. However the features of this reaction confirm the validity of our previously reported procedure for the synthesis of dialkyl and aryl alkyl disulfides.[1,3]

Experimental

All reactions were carried out in screw cap NMR sample tubes using $CDCl_3$ (kept over 13X molecular sieves), as solvent. Temperature was controlled by a glycol thermostatic bath. Thiolsulfonates **1b–e**,[8] disulfides **4b–e**[9] and **8a–e**,[9] thiosilanes **2b–e**[10] were synthesized using standard procedures, ^{13}C NMR spectra of all compounds were recorded before running the reactions (see below). Phenylthiotrimethylsilane **2a** was purchased from Aldrich and distilled before use. Methylthiotrimethylsilane **6**, diethyl disulfide **7a**, dimethyl disulfide **7b** and diphenyl disulfide **4a** were purchased from Aldrich and used without further purifications. TLC plates (Merck 60 F_{254}) were used for preparative TLC. GC–MS and GC–MS SIM spectra were performed with a Mass Selective Detector HP, 5970A. All ^1H NMR spectra were recorded at 200 MHz on a Varian Gemini 200; residual $CHCl_3$ was used as reference at 7.26 ppm. ^{13}C NMR spectra were recorded at 50 MHz and chemical shifts were referenced to the central line of the solvent ($CDCl_3$) at 77.00 ppm. A standard sequence was chosen to record ^{13}C NMR spectra used for quantitative analyses: spectral window 14 992.5 Hz, pulse width 45°, delay 15 s, transients 256, were typical parameters for samples at 0.6 mol dm^{-3} concentration of reagents.

Reaction of **2a** *with Thiosulfonates* **1**. *Standard Procedure.*—To a solution of thiolsulfonate (0.5 mmol) in $CDCl_3$ 0.7 cm^3 in a screw cap NMR sample tube, phenylthiotrimethylsilane (0.5 mmol) was added and the tube kept at 60 °C until complete disappearance of the reagents. The reaction mixture was diluted with $CHCl_3$ (10 cm^3) and washed with water (4 × 10 cm^3). The organic layer was dried over sodium sulfate and evaporated to dryness. The crude mixture was analysed by ^{13}C NMR spectroscopy and then purified by preparative TLC (eluent light petroleum:ethyl acetate, 20:1). ^1H and ^{13}C NMR spectroscopy were registered on the mixture of disulfides obtained after purification (only in the case of 4-methoxy derivatives was it possible to achieve separation of symmetrical and unsymmetrical disulfides) (see Table 1). Relevant ^{13}C NMR chemical shifts of thiolsulfonates **1c–e**, phenylthiotrimethylsilane **2a**, disulfides **3c–e** and **4c–e** are reported below; data for compounds **1b**, **3b** and **4b** have been published elsewhere.[3] Phenylthiotrimethylsilane **2a**: δ_C, 131.54 (C–SSi); 126.92 (C–H, *para*); 135.26, 128.83 (C–H). *S*-(4-Methoxyphenyl) 4-methoxybenzenethiosulfonate **1c**: δ_C, 163.69 (C–OMe, sulfonate part); 162.35 (C–OMe, thiol part); 134.83 (C *ipso*, sulfonate part); 118.82 (C *ipso*, thiol part); 138.38, 129.89, 114.92, 113.85 (C–H, both parts); 55.56 (CH_3–O, sulfonate part); 55.30 (CH_3–O, thiol part). *S*-(4-Chlorophenyl) 4-chlorobenzenethiosulfonate **1d**: δ_C, 141.37 (C, *ipso*, sulfonate part); 140.64 (C–Cl, sulfonate part); 138.63 (C–Cl, thiol part); 126.06 (C *ipso*, thiol part); 137.78, 129.99, 129.35, 128.99 (C–H, both parts). *S*-(4-Bromophenyl) 4-bromobenzenethiosulfonate **1e**: δ_C, 141.98, (C *ipso*, sulfonate part); 129.30 (C–Br, sulfonate part); 127.11, (C–Br, thiol part); 126.68 (C *ipso*, thiol part); 137.96, 133.03, 132.40, 129.04 (C–H, both parts). *4-Methoxyphenyl phenyl disulfide* **3c**: δ_C, 160.00 (C–OMe); 137.60 (C *ipso*, unsubstituted part); 128.11, (C *ipso*, substituted part); 127.31 (C–H, *para*); 131.87, 129.11, 128.30, 114.76 (C–H, both parts); 55.16 (CH_3–O). 4-Chlorophenyl phenyl disulfide **3d**: δ_C, 136.88 (C *ipso*, substituted part); 135.74 (C *ipso*, unsubstituted part); 133.38 (C–Cl); and 127.54 (C–H, *para*); 129.30, 129.10, 127.86 (C–H, both parts). 4-Bromophenyl phenyl disulfide **3e**: δ_C, 136.59 (C *ipso*, unsubstituted part); 136.37, (C *ipso*, substituted part), 121.21 (C–Br), 127.52 (C–H, *para*), 132.17, 129.24, 129.17, 127.78 (C–H, both parts). Bis(4-methoxyphenyl) disulfide **4c**: δ_C, 160.09 (C–OMe), 128.49 (C *ipso*), 132.74, 114.66 (C–H), 55.22 (CH_3–O). Bis(4-Chlorophenyl) disulfide **4d**: δ_C, 135.25 (C *ipso*), 133.72 (C–Cl), 129.39 (C–H, coincidents). Bis(4-bromophenyl) disulfide **4e**: δ_C, 135.85 (C *ipso*), 121.62 (C–Br), 132.33, 129.48 (C–H).

Thermal Stability of Symmetrical Disulfides **4**.—Equimolar amounts of **4a** and **4d**, or **4a** and **4e** (0.42 mmol) in $CDCl_3$ (0.7 cm^3) were heated at 60 °C for 24 h. ^{13}C NMR spectra of the reaction mixtures showed no formation of unsymmetrical species **3d** in the former case, while 5% of 4-bromophenyl phenyl disulfide **3e** was detected in the second case.

Exchange Reaction between Disulfides and Thiosilanes: Standard Procedure.—To a solution of disulfide (0.42 mmol) in $CDCl_3$ (0.7 cm^3) in a screw cap NMR sample tube, the thiosilane (0.42 mmol) was added. The mixture was heated at

60 °C and analysed by ^1H and or ^{13}C NMR spectroscopy to evaluate its composition.

Reaction of phenylthiotrimethylsilane **2a** *with diaryl disulfides:* (*a*) *reaction with bis*(4-*methoxyphenyl*) *disulfide* **4c**. After 27 h ^{13}C NMR analysis showed the presence, together with the starting materials, of: 4-methoxyphenyl phenyl disulfide **3c**, diphenyl disulfide **4a**, 4-methoxyphenylthiotrimethylsilane **2c** (see Table 2). *2c*: δ_C, 158.80 (C–OMe), 121.43 (C–SSi), 136.22, 116.27 (C–H), 55.13 (CH_3–O), 0.66 (CH_3–Si).

(*b*) *Reaction of* **2a** *with bis*(4-*chlorophenyl*) *disulfide* **4d**. After 27 h ^{13}C NMR analysis showed the presence, together with the starting materials, of: 4-chlorophenyl phenyl disulfide **3d**, diphenyl disulfide **4a**, 4-chlorophenylthiotrimethylsilane **2d** (see Table 2). **2d**: δ_C, 133.09 (C–Cl), 130.07 (C–SSi), 136.27, 128.83 (C–H), 0.75 (CH_3–Si).

Reactions of silanes **2a–c** *and* **2e** *with alkyl aryl disulfides* **8**. Reactions were run under the general conditions described above. In all these cases it has been possible to analyse the reaction mixtures by ^1H NMR spectra. In any case the absence of the diaryl products was confirmed by ^{13}C NMR and GC–MS techniques. Composition of individual reaction mixtures is reported in Scheme 8. Relevant ^1H NMR chemical shifts of species not previously described are as follows: 4-Methylphenylthiotrimethylsilane **2b**: δ_H, 2.33 (CH_3–Ph) 0.10 (CH_3–Si). 4-Methoxyphenylthiotrimethylsilane **2c**: δ_H, 3.77 (CH_3O), 0.25 (CH_3–Si). 4-Bromophenylthiotrimethylsilane **2e**: δ_H, 0.29 (CH_3–Si). 4-Methylphenyl methyl disulfide **8c**: δ_H, 2.44 (CH_3–S), 2.35 (CH_3–Ph). 4-Methoxyphenyl methyl disulfide **8d**: δ_H, 3.82 (CH_3–O); 2.44 (CH_3–S). 4-Bromophenyl methyl disulfide **8e**: δ_H, 2.45 (CH_3–S).

Reaction of thiosilane [$^2H_5$]**2a** *with phenyl methyl disulfide* **8b**. Synthesis of [$^2H_5$]phenylthiotrimethylsilane was achieved by chlorosulfonation of hexadeuteriobenzene with $ClSO_3H$; lithium aluminium hydride reduction of the sulfonyl chloride obtained gave [$^2H_5$]thiophenol which was converted into [$^2H_5$]phenylthiotrimethylsilane [$^2H_5$]**2a** by a standard procedure.[10a] A mixture of [$^2H_5$] **2a** (66 mg, 0.35 mmol) and **8b** (55 mg, 0.35 mmol) in $CDCl_3$ (0.7 cm^3) in a screw cap NMR sample tube was heated at 60 °C for 42 h. The mixture was then analysed by means of GC–MS SIM methodology. The ion at *m*/*z* 80 in the spectrum of thiosilanes was chosen for quantitative analysis. This ion was present as 1% of the total ion current in the spectra of undeuteriated species and was detected as 18.5% of total current in the deuteriated species before reaction. The reaction mixture analysed after 42 h showed the occurrence of the selected ion in the thiosilanes spectrum as 16% of the total ion current. This data indicates that thiosilanes were composed of 86% of deuteriated species and 14% of exchanged phenylthiosilane **2a**.

Reaction of **2a** *with dimethyl disulfide* **7b**. The reaction was heated for 250 h at 60 °C. ^1H NMR analysis using the different chemical shift values of the methyl and trimethylsilyl groups showed the presence of: dimethyl disulfide **7b**: (δ_H 2.39, CH_3–S), 25%; phenylthiotrimethylsilane **2a**: (δ_H 0.27, CH_3–Si), 25%; methylthiotrimethylsilane **6**: (δ_H 1.99, CH_3–S; 0.31, CH_3–Si), 25%; phenyl methyl disulfide **8b**: (δ_H 2.41, CH_3–S) 25%.

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