[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF IOWA STATE COLLEGE AND TUSKEGEE INSTITUTE]

The Synthesis of (Arylthioalkyl)- and (Arylsulfonylalkyl)-silanes

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As reported earlier, certain aryl methyl sulfides and sulfones undergo lateral metalation with *n*-butyllithium in ether. Also, methyl-*p*-tolylsulfone reacts with alkyl Grignard reagents yielding *p*-toluenesulfonylmethylmagnesium halides. The resultant arylthio- and arylsulfonylmethyllithium and arylsulfonylmethylmagnesium halides are capable of forming substituted sulfur-containing silanes by coupling with ethoxy- and chlorosilanes. The preparation of some β-arylthioethyl- and β-arylsulfonylethyltriphenylsilanes by the addition of thiols to triphenylvinylsilane and the subsequent peracetic acid oxidation is also described.

The object of this investigation was to introduce the sulfide or sulfone group into alkyl- and arylalkylsilanes for the purpose of examining the effects of these groups and their positions, with relation to the silicon atom, on the stability of the carbon–silicon bond toward acidic, basic and oxidizing agents. This report primarily concerns the syntheses of these silanes.

In the syntheses of some of the sulfur-containing silanes, advantage was taken of two reactions reported earlier: (1) the lateral metalation of methyl aryl sulfides and sulfones with *n*-butyllithium in ether[2a,b]

$$RSCH_3 + n\text{-}C_4H_9Li \longrightarrow RSCH_2Li + nC_4H_{10} \quad (1)$$

and (2) the formation of *p*-toluenesulfonylmethylmagnesium bromide from *p*-tolyl methyl sulfone and an alkyl Grignard reagent.[3a,b]

$$p\text{-}C_7H_7SO_2CH_3 \xrightarrow{RMgBr} [p\text{-}C_7H_7SO_2CH_2]MgBr \quad (2)$$

These metalation products are capable of reacting with chloro- or alkoxysilanes according to the schemes

$$\left.\begin{array}{l} p\text{-}C_7H_7SO_2CH_2Li \\ {[p\text{-}C_7H_7SO_2CH_2]MgX} \end{array}\right] \xrightarrow{R_3SiCl} R_3SiCH_2SO_2C_7H_7\text{-}p \quad (3)$$

$$p\text{-}C_7H_7SCH_2Li \xrightarrow{R_3SiCl} R_3SiCH_2SC_7H_7\text{-}p$$

$$4RSCH_2Li + (C_2H_5O)_4Si \longrightarrow (RSCH_2)_4Si + 4C_2H_5OLi \quad (4)$$

In the subsequent reactions of the newly formed organometallic compounds with trimethyl- and triphenylchlorosilane, the arylsulfonylmethyllithium was superior in reactivity to the corresponding Grignard reagent. Also, it is of interest to note that no definite product could be isolated from the reaction of *p*-toluenesulfonylmethyllithium with trimethylchlorosilane although a 78% yield of the expected coupling product, trimethyl-(*p*-toluenethiomethyl)-silane, was produced from *p*-toluenethiomethyllithium and the chlorosilane. Moreover, the corresponding sulfone could not be secured from the hydrogen peroxide oxidation of the sulfide. Results of these investigations are summarized in Table I.

TABLE I

REACTION OF LATERALLY METALATED SULFUR COMPOUNDS WITH CHLOROSILANES AND TETRAETHOXYSILANE

Metalation product	Silane	Yield of product,[a] %
$[p\text{-}C_7H_7SO_2CH_2]MgI$	$(CH_3)_3SiCl$	0
$[p\text{-}C_7H_7SO_2CH_2]MgBr$	$(C_6H_5)_3SiCl$	12
$p\text{-}C_7H_7SO_2CH_2Li$	$(C_6H_5)_3SiCl$	31
$p\text{-}C_7H_7SO_2CH_2Li$	$(CH_3)_3SiCl$	0
$p\text{-}C_7H_7SCH_2Li$	$(CH_3)_3SiCl$	78
$p\text{-}C_7H_7SCH_2Li$	$(C_6H_5)_3SiCl$	67[b]
$C_6H_5SCH_2Li$	$(C_2H_5O)_4Si$	42
$p\text{-}C_7H_7SCH_2Li$	$(C_2H_5O)_4Si$	53[c]

[a] Based on the original amount of chloro- or ethoxysilane. [b] 73% based on the unrecovered sulfide. [c] Crude yield, 71%.

The mode of peroxide-catalyzed addition of thiols to olefins was established by Kharasch and his associates[4] and, while this study was in progress, Burkhard[5] proved that the normal course of addition is followed when thiols react with alkenylsilanes. We found that in the presence of benzoyl peroxide and at slightly elevated temperatures, benzenethiol, *p*-toluenethiol, and α-toluenethiol readily add to triphenylvinylsilane. The resultant triphenyl-(β-arylthioethyl)-silanes were easily oxidized to the corresponding sulfones by peracetic acid.

$$(C_6H_5)_3SiCH{=}CH_2 \xrightarrow{RSH} (C_6H_5)_3SiCH_2CH_2SR \xrightarrow[CH_3COOH]{H_2O_2} (C_6H_5)_3SiCH_2CH_2SO_2R \quad (5)$$

In previous work,[6] it has been shown that in certain substituted alkyl silanes the Si–C bond is weakened by the presence of functional groups in the *beta* and *gamma* positions (with reference to the silicon atom). Recent studies[5] have indicated that this linkage is unaffected by the presence of a sulfur atom in the *delta* position as evidenced by the stability of these sulfur-containing silanes in the presence of alcoholic caustics. It has been shown,[7] however, that the Si–C bond in 2-, 3- and 4-trimethylsilyldibenzothiophene is ruptured by the prolonged action of hydrogen chloride in glacial acetic acid whereas the "so-called" negative sulfonyl group of the corresponding trimethylsilyldibenzothiophene-5-dioxides is without significant influence on the rate of cleavage of the Si–C bond. Results of cleavage studies on the sulfides and sulfones described in this paper will be reported later.

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[1] Frederick Gardner Cottrell Fellow, George Washington Carver Foundation, Tuskegee Institute, Alabama (1950–1952).

[2] (a) H. Gilman and F. J. Webb, THIS JOURNAL, **62**, 987 (1940); *ibid.*, **71**, 4062 (1949); (b) see also, Webb, Doctoral Dissertation, Iowa State College, 1940.

[3] (a) W. M. Ziegler and R. Connor, THIS JOURNAL, **62**, 2596 (1940). (b) After the completion of this work, it was reported that α-halomagnesium derivatives of sulfones show the typical reaction of Grignard reagents with benzaldehyde [L. Field, *ibid.*, **74**, 3919 (1952)].

[4] M. S. Kharasch, A. T. Read and F. R. Mayo, *Chemistry and Industry*, **57**, 752 (1938); F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 387 (1940).

[5] C. A. Burkhard, THIS JOURNAL, **72**, 1078 (1950).

[6] H. Gilman and F. J. Marshall, *ibid.*, **71**, 2066 (1949). References to earlier cleavage studies are summarized in this paper.

[7] H. Gilman and J. F. Nobis, *ibid.*, **72**, 2629 (1950); G. Illuminati, J. F. Nobis and H. Gilman, *ibid.*, **73**, 5887 (1951).

TABLE II

SULFIDES (A) AND SULFONES (B) FROM THE ADDITION OF THIOLS TO TRIPHENYLVINYLSILANE AND SUBSEQUENT OXIDATION

R	Yield, %	M.p., °C.[a]	Formula	S analysis, %[b] Calcd.	S analysis, %[b] Found	Si analysis, %[c] Calcd.	Si analysis, %[c] Found
			(A) $(C_6H_5)_3SiCH_2CH_2SR$				
C_6H_5	65[d]	99-100	$C_{26}H_{24}SSi$	8.08	8.24	7.08	7.26
p-C_7H_7	57[e,f]	97-99	$C_{27}H_{26}SSi$	7.81	7.56	6.83	6.83
$C_6H_5CH_2$	18[g]	72-73	$C_{27}H_{26}SSi$	7.81	7.66	6.83	7.07
			(B) $(C_6H_5)_3SiCH_2CH_2SO_2R$				
C_6H_5	85	155	$C_{26}H_{24}O_2SSi$	7.48	7.38	6.55	6.61
p-C_7H_7	83	152	$C_{27}H_{26}O_2SSi$	7.24	7.10	6.34	6.37
$C_6H_5CH_2$	75	153-154	$C_{27}H_{26}O_2SSi$	7.24	7.12	6.34	6.54

[a] The melting points are uncorrected. [b] Sulfur analyses were made by the macro Parr bomb method. [c] The procedure of H. Gilman, *et al.*, THIS JOURNAL, 72, 5767 (1950), was followed. [d] Recrystallized from ethanol. [e] The reactants were heated together in the absence of a solvent for 24 hr. on an oil-bath maintained at 160–165°. [f] Recrystallized from a mixture of ethanol and 1-propanol. [g] The recrystallization solvent was a mixture of methanol, 95% ethanol and *n*-butyl acetate.

Experimental

Reaction of Trimethylchlorosilane with *p*-Toluenesulfonylmethylmagnesium Iodide.—To a solution of 0.025 mole of methylmagnesium iodide in 30 ml. of ether there was gradually added with stirring 5.1 g. (0.03 mole) of methyl *p*-tolylsulfone[8] in 30 ml. of benzene.[3a] After the evolution of methane had ceased, Color Test I[9] was positive, so the mixture was refluxed for 20 minutes during which time a precipitate formed but gradually redissolved. Then, 3.8 ml. (3.2 g., 0.03 mole) of trimethylchlorosilane was added to the reaction mixture (Color Test I was negative), and stirring was continued for 2 hours. Hydrolysis of the magnesium complex was carried out in the usual manner, and after working up the ether extract, the only product isolated was 1.5 g. (23%) of the unchanged sulfone (m.p. and mixed m.p. 85–86°).

In a second attempt, ethylmagnesium bromide was used, and after the addition of the silane, the reaction mixture was stirred and refluxed for 42 hours. The solid formed was removed by filtration and washed with several portions of warm benzene. After concentrating the combined filtrates, no identifiable product could be isolated.

Triphenyl-(*p*-toluenesulfonylmethyl)-silane. A. **From Triphenylchlorosilane and *p*-Toluenesulfonylmethylmagnesium Bromide.**—To a suspension of *p*-toluenesulfonylmethylmagnesium bromide[3a] prepared from 0.03 mole of ethylmagnesium bromide in 40 ml. of benzene there was added 9.0 g. (0.03 mole) of triphenylchlorosilane in 50 ml. of ether. After distilling approximately two-thirds of the ether and replacing it with an equivalent volume of benzene, refluxing was continued for 18 hours. Approximately 5 g. of inorganic solids separated from the reaction mixture, and from the ether–benzene solution there was obtained 6 g. (66%) of crude triphenylchlorosilane (melting over the range of 70–90°) and 1.5 g. (12% based on the original amount of triphenylchlorosilane) of triphenyl-(*p*-toluenesulfonylmethyl)-silane; m.p. 173–174° (from a mixture of ligroin and benzene).

B. **From Triphenylchlorosilane and *p*-Toluenesulfonylmethyllithium.**—To 300 ml. of a solution of *p*-toluenesulfonylmethyllithium[2a] prepared by metalating 5.1 g. (0.03 mole) of methyl *p*-tolylsulfone with 0.03 mole of *n*-butyllithium[10] there was added 8.5 g. (0.03 mole) of triphenylchlorosilane in 60 ml. of ether. The reaction mixture was stirred for 12 hours at room temperature and then refluxed for 1 hour. After this time, Color Test I was negative. The inorganic material was removed by suction filtration and washed with warm benzene. From the filtrate and washings there was obtained 6 g. of a crude mixture of the unchanged sulfone and triphenylchlorosilane with 4 g. (31%) of triphenyl-(*p*-toluenesulfonylmethyl)-silane; m.p. and mixed m.p. with the product from **A** was 175°.

Anal. Calcd. for $C_{26}H_{24}O_2SSi$: Si, 6.54. Found: Si, 6.63.

Tetra-(benzenethiomethyl)-silane.—The lateral metalation of 18 g. (0.15 mole) of methyl phenyl sulfide[11] with 0.15 mole of *n*-butyllithium was accomplished following a procedure described in the literature.[2a] To the solution of benzenethiomethyllithium there was added while stirring 8 g. (0.04 mole) of tetraethoxysilane at such a rate as to maintain steady refluxing of the solvent. Color Test I was positive immediately after the addition of the silane, but became negative after stirring the reaction mixture for an additional half hour. After this time, the contents of the flask were poured onto cracked ice, and the ether layer was separated, washed with water, then dried over anhydrous calcium chloride. After removing the excess solvent, there was recovered from the residue 6.7 g. (37%) of methyl phenyl sulfide and 8.1 g. (42%) of the product. The pure substance melted at 67–69° after recrystallization from a mixture of ethyl acetate and ethanol.

Anal. Calcd. for $C_{28}H_{28}S_4Si$: S, 24.61; Si, 5.38. Found: S, 24.20; Si, 5.78.

Tetra-(*p*-toluenethiomethyl)-silane.—The procedure employed in the preparation of this compound was essentially the same as the one described above. From 21 g. (0.15 mole) of methyl *p*-tolyl sulfide, 0.15 mole of *n*-butyllithium, and 8 g. (0.04 mole) of tetraethoxysilane there resulted 15.1 g. (71%) of the crude product. Eleven and two-tenths grams (53%) of the pure product melting at 70° was obtained after recrystallization from a mixture of ethyl acetate and ethanol or from ligroin. Eight grams (38%) of the original sulfide was also recovered from the reaction.

Anal. Calcd. for $C_{32}H_{36}S_4Si$: S, 22.22; Si, 4.85. Found: S, 21.98; Si, 4.80.

Triphenyl-(*p*-toluenethiomethyl)-silane.—*p*-Toluenethiomethyllithium was prepared from 0.058 mole of *n*-butyllithium in 150 ml. of ether and 9 g. (0.065 mole) of methyl *p*-tolyl sulfide. To this solution there was added dropwise 14 g. (0.05 mole) of triphenylchlorosilane in 75 ml. of ether. (Color Test I was negative.) The hydrolysis of any excess organometallic compound was carried out in the usual manner, whereupon most of the pure product settled out at the water–ether interface. The yield of the pure material was 13.3 g. (67% based on the original amount of triphenylchlorosilane used, and 73% based on the unrecovered sulfide); m.p. 148–149°. Two and seven-tenths grams of the unchanged sulfide was recovered.

Anal. Calcd. for $C_{26}H_{24}SSi$: Si, 7.08. Found: Si, 6.99.

Trimethyl-(*p*-toluenethiomethyl)-silane.—Eleven grams (0.08 mole) of methyl *p*-tolyl sulfide was metalated with 0.08 mole of *n*-butyllithium. Into the resulting solution (150 ml.) there was gradually introduced 10.7 ml. (8.7 g., 0.08 mole) of trimethylchlorosilane. After stirring and refluxing for one-half hour, Color Test I was negative. Subsequent to hydrolysis the ether layer was separated, washed with water, and dried over anhydrous calcium chloride. From this reaction there was isolated 2.8 g. (25%) of the original sulfide and 13.2 g. (78%) of the product; b.p. 83–85° (1 mm.), n^{20}_{D} 1.5356, d^{20}_{20} 0.9545.

Anal. Calcd. for $C_{11}H_{18}SSi$: S, 15.24; *MR*D,[12] 67.84. Found: S, 15.20; *MR*D, 68.58.

Triphenyl-(β-benzenethioethyl)-silane.—The following procedures are typical for the preparation of the sulfides and sulfones listed in Table II. A solution of 5 g. (0.018 mole) of triphenylvinylsilane,[13] 2.5 g. (0.022 mole) of thiophenol, and 0.1 g. of benzoyl peroxide in 30 ml. of glacial acetic acid was refluxed for 20 hours. After cooling, this solution was diluted with water and neutralized with 10% sodium hydroxide. The oil was extracted with ether and dried over anhydrous calcium chloride. After removing the ether by distillation, the residue was crystallized by cooling and triturating. The pure product was secured by recrystallization from ethanol.

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(8) R. Otto, *Ber.*, **18**, 154 (1885).

(9) H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

(10) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, *ibid.*, **71**, 1499 (1949).

(11) J. W. Baker and W. G. Moffitt, *J. Chem. Soc.*, 1722 (1930).

(12) The values for the group and bond refractions were taken in part from E. L. Warrick, *ibid.*, **68**, 2455 (1946), and R. O. Sauer, *ibid.*, **68**, 954 (1946).

(13) L. F. Cason and H. G. Brooks, *ibid.*, **74**, 4582 (1952).

Triphenyl-(β-benzenesulfonylethyl)-silane.—A solution of 2.73 g. (0.007 mole) of triphenyl-(β-benzenethioethyl)-silane, 58 ml. (0.47 mole) of 30% hydrogen peroxide and 90 ml. of glacial acetic acid was allowed to stand for 24 hours at room temperature and then refluxed for 45 minutes. On cooling, the pure sulfone crystallized from the solution.

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Analogs of Hexaphenylethane. I. Hexaaryldisilanes Containing Phenyl and *p*-Tolyl Groups

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A complete series of ten hexaaryldisilanes containing phenyl and *p*-tolyl groups has been prepared. They were made by coupling a triarylsilylpotassium compound with a triarylchlorosilane; by treating a partially chlorinated organodisilane with an organolithium compound; or by coupling a triarylchlorosilane with sodium. Examination of these compounds shows that, in general, as the degree of symmetry of the disilane decreases the melting point decreases and the solubility increases. The possible dissociation of these hexaaryldisilanes is discussed.

It is known that hexaarylethanes dissociate to give triarylmethyl radicals. However, similar dissociation of hexaaryldisilanes have not been observed.[2,3] One of the difficulties in detecting the degree of dissociation of the hexaarydisilanes is due to the extremely small solubilities in ordinary organic solvents. Accordingly, we prepared a number of hexaaryldisilanes containing two kinds of aryl groups in different positions of the molecules in order to study their solubilities in relation to their structures. There are ten possible structures of hexaaryldisilanes containing phenyl and *p*-tolyl groups. Among them only the simple symmetrical hexaphenyl-[3] and hexa-*p*-tolyldisilane[4] have been described. These two compounds are high-melting solids having low solubilities in most organic solvents.

The new disilanes containing both phenyl and *p*-tolyl groups are lower melting solids with improved solubilities. In general, the less symmetrical the disilane is, the lower is the melting point and the higher is the solubility. Thus, while the simple symmetrical hexaphenyldisilane and hexa-*p*-tolyldisilane melt over 350°, the unsymmetrical 1,1,2-triphenyl-1,2,2-tri-*p*-tolyldisilane melts at 226–227°. It is interesting to observe that although the symmetrical tetraphenyldi-*p*-tolyldisilane has a higher melting point than the unsymmetrical isomer as one might have expected, the melting points of both the symmetrical and unsymmetrical diphenyltetra-*p*-tolyldisilanes are the same. Furthermore, a mixed melting point determination of these two diphenyltetra-*p*-tolyldisilanes showed no depression. The melting points of the hexaaryldisilanes are summarized in Table I.

No quantitative determinations of the solubilities of the hexaaryldisilanes were made in this investigation. However, the solubilities appear to increase with decreasing degree of symmetry of the disilanes. For example, hexaphenyldisilane is only moderately soluble in hot xylene while 1,1,2-triphenyl-1,2,2-tri-*p*-tolyldisilane is very soluble in benzene even at room temperature. The solubilities of these disilanes in various solvents are also given in Table I.

The hexaaryldisilanes described in this paper were prepared by methods outlined below.

$$2R'R''R'''SiCl + 2Na \longrightarrow (R'R''R''')_2Si_2 \quad (1)$$

$$R'R''R'''SiCl + R^{IV}R^{V}R^{VI}SiK \longrightarrow R'R''R'''SiSiR^{IV}R^{V}R^{VI} \quad (2)$$

$$R_3SiSiCl_3 + 3R'Li \longrightarrow R_3SiSiR_3' \quad (3)$$

$$R_3SiSiRCl_2 + 2R'Li \longrightarrow R_3SiSiRR'_2 \quad (4)$$

$$R_3SiSiR_2Cl + R'Li \longrightarrow R_3SiSiR_2R' \quad (5)$$

In the above equations the R's represent phenyl or *p*-tolyl groups, as the case may be. A few disilanes were prepared by two different methods to confirm their structures. Three new chlorine-containing organosilicon compounds were prepared in order to synthesize the disilanes. These are phenyldi-*p*-tolylchlorosilane, 1,1,1-triphenyl-2,2,2-trichlorodisilane and 1,1,1,2-tetraphenyl-2,2-dichlorodisilane. They were made according to the equations

$$C_6H_5SiCl_3 + 2p\text{-}CH_3C_6H_4Li \longrightarrow (C_6H_5)(p\text{-}CH_3C_6H_4)_2SiCl \quad (6)$$

$$(C_6H_5)_3SiK + SiCl_4 \longrightarrow (C_6H_5)_3SiSiCl_3 \quad (7)$$

$$(C_6H_5)_3SiK + C_6H_5SiCl_3 \longrightarrow (C_6H_5)_3SiSi(C_6H_5)Cl_2 \quad (8)$$

It was observed that the coupling reactions of triarylsilylpotassium compounds with triarylchlorosilanes give better yields than the reactions between an aryllithium compound with a partially chlorinated organodisilane such as pentaphenylchlorodisilane (compare Table I). This is probably due to the ease of cleavage of the chlorinated organodisilanes. The ease of cleavage of hexachlorodisilane has been observed previously. When octachlorotrisilane is treated with phenylmagnesium bromide the products obtained are hexaphenyldisilane and tetraphenylsilane instead of octaphenyltrisilane[4] although the trisilane can be prepared by the reaction of triphenylsilylpotassium with diphenyldichlorosilane.[5] We have also observed that a considerable amount of tetra-*p*-tolylsilane was formed when hexachlorodisilane was treated with *p*-tolyllithium.

The possible dissociation of the hexaaryldisilanes was studied by the treatment of 1,1,2-triphenyl-

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