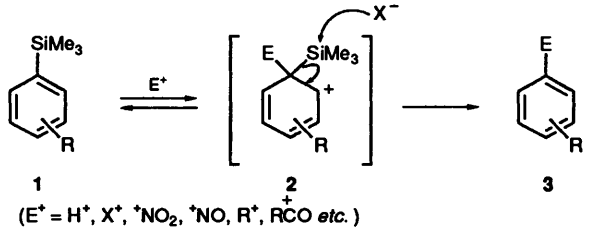
Deprotonative Friedel–Crafts Alkylation of Arylsilanes with α-Chlorosulfides

Hiroyuki Ishibashi,* Hiroshi Sakashita and Masazumi Ikeda *
Kyoto Pharmaceutical University, Misasagi, Yamashina, Kyoto 607, Japan

Friedel–Crafts alkylation of trimethylphenylsilane with methyl chloro(methylthio)acetate in the presence of tin(IV) chloride gave a mixture of three regioisomers of methyl 2-(trimethylsilylphenyl)-2-(methylthio)acetates in which the *meta*- and *para*-isomers predominated. No *ipso*-substitution product was obtained. Based on the isomer distribution, the relative reactivity of the phenylsilane to benzene and the effects of the substituents on the orientation, it was suggested that in the Friedel–Crafts alkylation the trimethylsilyl group is a very slightly activating substituent on the benzene ring but has essentially no directing effect.

Electrophilic substitution reactions of arylsilanes **1** are well known to give the products **3** in which the electrophile occupies the position to which the silyl group was originally bonded (*ipso*-substitution).[1–3] These reactions are formulated as proceeding *via* delocalized cationic intermediates **2** stabilised by the β-carbon–silicon bond. Nevertheless, a limited number of the normal (protonative) electrophilic substitution reactions have been reported, which include nitration,[4] chlorination,[5] and a Friedel–Crafts alkylation with dichloromethyl methyl ether.[6] All of them are accompanied, more or less, by desilylative substitution reactions. It is suggested that the trimethylsilyl (TMS) group is a very weak activating and *ortho–para* directing substituent in chlorination and nitration.



Scheme 1

During the course of our investigation of the electrophilic substitution reactions of arenes with α-chlorosulfides,[7] we found that trimethylphenylsilane **4** undergoes a deprotonative Friedel–Crafts alkylation with methyl chloro(methylthio)-acetate **5** to give the *meta*- and *para*-substituted phenylsilanes **6** as the major products.[8] Since this is the first reported example of a deprotonative Friedel–Crafts alkylation of arylsilanes where no desilylative (*ipso*-substitution) product was observed, we have investigated this reaction in more detail. In this paper we discuss the effects of the TMS group in the Friedel–Crafts alkylation of the phenylsilanes, based on the product distribution, the relative reactivity of the phenylsilane **4** to benzene as well as the effects of substituents upon orientation.

Results and Discussion

When trimethylphenylsilane **4** (5 equiv.) was treated with the α-chlorosulfide **5** (1 equiv.) in the presence of tin(IV) chloride (1 equiv.)† in dichloromethane at room temperature for 30 min, a mixture of three regioisomers of methyl 2-methylthio-2-(trimethylsilylphenyl)acetates **6** was produced in 54% yield (based on the chlorosulfide **5**). A combination of a GLC analysis and desulfurisation of **6** showed it to be a mixture of the *ortho*-, *meta* and *para*-isomers in a ratio of 4:67:29. Desulfurisation of **6** with Raney nickel gave a mixture of methyl (trimethylsilylphenyl)acetates **7**, the structures of which were confirmed by a GLC comparison with authentic samples prepared from the respective trimethyltolylsilanes.[9] It is of interest to note that no *ipso*-substitution product **8** was detected in the reaction mixture.

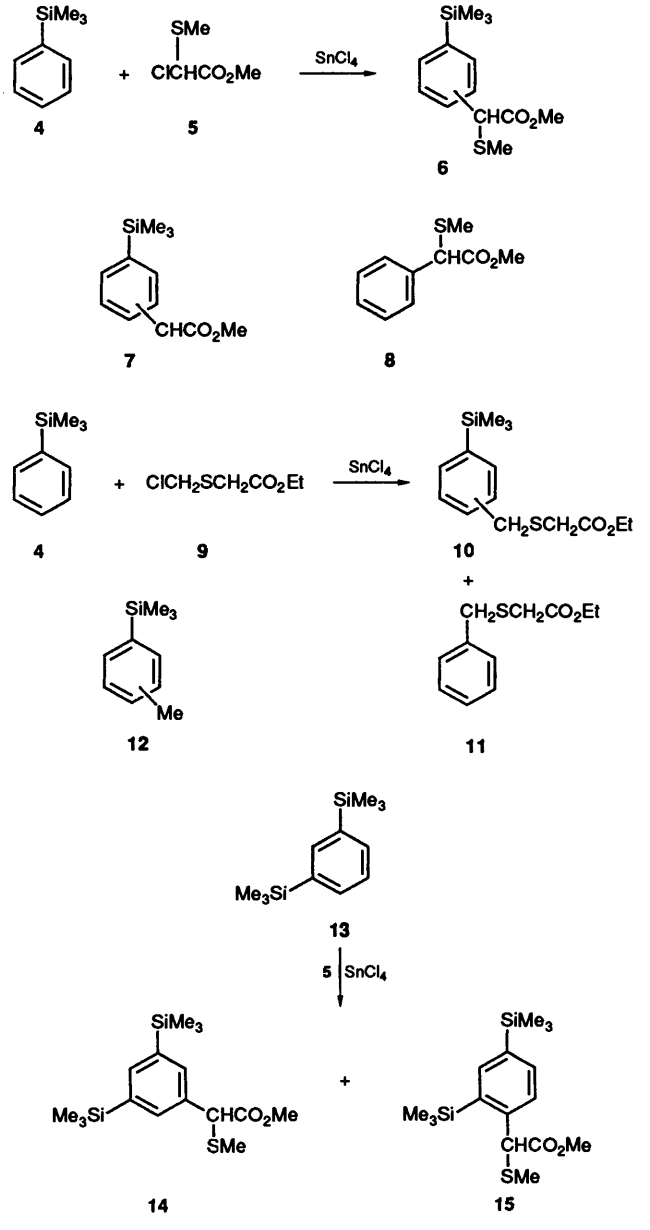
The reaction of **4** with ethyl (chloromethylthio)acetate **9**[10] in the presence of tin(IV) chloride at room temperature for 7 h afforded the alkylated products **10** and the *ipso*-substitution product **11** in 41 and 20% yields (based on the chlorosulfide **9**), respectively. The alkylated products **10** were found to be a mixture of three regioisomers (*ortho*:*meta*:*para* = 3:71:26). Desulfurisation of **10** with Raney nickel gave a mixture of trimethyltolylsilanes **12**, the structures of which were assigned by a GLC comparison with authentic samples prepared from the respective halogenotoluenes.[9] When the reaction was terminated after a short period (2.5 h), an almost identical ratio of the products **10** (36%) and **11** (15%) was obtained, suggesting that the latter is formed by desilylative Friedel–Crafts reaction (*ipso*-substitution) of **4** and not by protodesilylation of **10**.

1,3-Bis(trimethylsilyl)benzene **13**, on treating with the α-chlorosulfide **5** in the presence of tin(IV) chloride, afforded an inseparable mixture of the alkylated products **14** and **15** in a ratio of *ca.* 90:10. Although the structure of **14** was readily assigned on the basis of the ^{1}H NMR spectrum (see Experimental section), that of the minor product is only speculative due to the small amount obtained.

The lack of the *ipso*-substitution products in the reaction of the phenylsilane **4** with the α-chlorosulfide **5** may be attributed to the steric repulsion between the TMS group and the bulky complex **A** formed from **5** and the Lewis acid, in the transition state leading to the intermediate **B** (Scheme 3). This view was supported by the fact that the reaction of **4** with the primary chloride **9** gave a considerable amount (20%) of the *ipso*-substitution product **11**.

Based on well documented examples of the formation of relatively large amounts of the *meta*-isomer in the Friedel–Crafts alkylation of toluene with benzyl bromide in the presence of $GaBr_3$[11] and a Lewis acid-catalysed isomerisation of dialkylbenzenes,[12] one might predict that the *para*-isomer of **6** would be in an equilibrium with the *meta*-isomer of **6** under the reaction conditions. However, this possibility is ruled out by the following observations. The previous studies[13] revealed that the Friedel–Crafts alkylation of arenes with the α-chlorosulfides

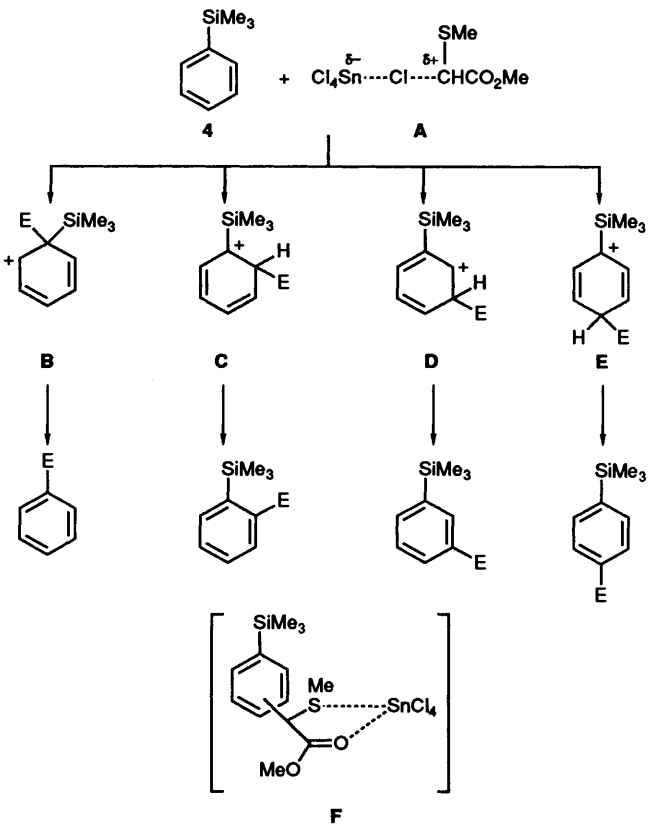
† Use of equimolar amounts of **4** and **5** resulted in a decrease in the total yield of **6** and an increase in the formation of methyl bis(methylthio)-acetate as a by-product.



Scheme 2

requires 1 equiv. of a Lewis acid and gives no polyalkylation products. These results have been explained by assuming that the Lewis acid forms the complex **F** with the alkylated product, which deactivates the aromatic ring toward further substitution. Further support for the view that this alkylation is kinetically controlled, was given by the fact that the reaction time (5 min or 30 min at room temperature) had little effect on the proportions of the products in the reaction of **4** with **5**, and that treatment of the alkylated products **6** with trifluoroacetic acid in carbon tetrachloride[14] under reflux for 10 h gave rise only to the desilylated product **8**.

In order to determine the reactivities of the phenylsilane **4** relative to benzene, competitive alkylations have been carried out. The relative reactivity of **4** over benzene was determined by treating equimolar amounts of the two aromatics in a dichloromethane solution at 20 °C. However, it was difficult to obtain accurate results for competitive alkylation of toluene and benzene, because toluene reacted too quickly. Therefore, the relative reactivity of toluene over benzene was calculated from that of the phenylsilane **4** over toluene. These results, together with the isomer distributions of the alkylated products



Scheme 3

and partial rate factors are summarised in Table 1. A comparison of k(phenylsilane)/k(benzene) with k(toluene)/k(benzene) indicates that the TMS group is a very slight activating substituent on the benzene ring. This would be a reflection of weak electron-donating properties of the TMS group, which result from cancellation of the inductive electron donation by $(p\text{–}d)_\pi$ back-bonding electron withdrawal.[15]

The partial rate factors[16,17] of the phenylsilane **4** for the alkylation imply that the TMS group slightly activates both the *meta*-* and *para*-positions in the phenyl ring, compared with benzene.† However, if one compares the TMS group with the methyl group, this activating effect is very weak. Furthermore, this alkylation is relatively unselective and the substitution takes place at the *meta*- and *para*-positions on an almost statistical basis. It is concluded that the TMS group has essentially no directing effect. The *ortho*-position seems to be sterically influenced by the TMS group.

We were then led to investigate the effect of the substituents on the orientation in this reaction (Scheme 4). Thus, reaction of trimethyl-*m*-tolylsilane **16** with the α-chlorosulfide **5** gave **17a** (36% isolated yield), **17b** (36%) (**17a**:**17b** = 41:59‡ determined

* It should be emphasised that an argument that the transition state leading to the intermediate **C** for the *meta*-attack is stabilised by the silyl group β to carbenium ion centre is not applicable in this case, since the coplanarity of the carbon–silicon bond and the vacant p-orbital cannot be achieved in such a species.

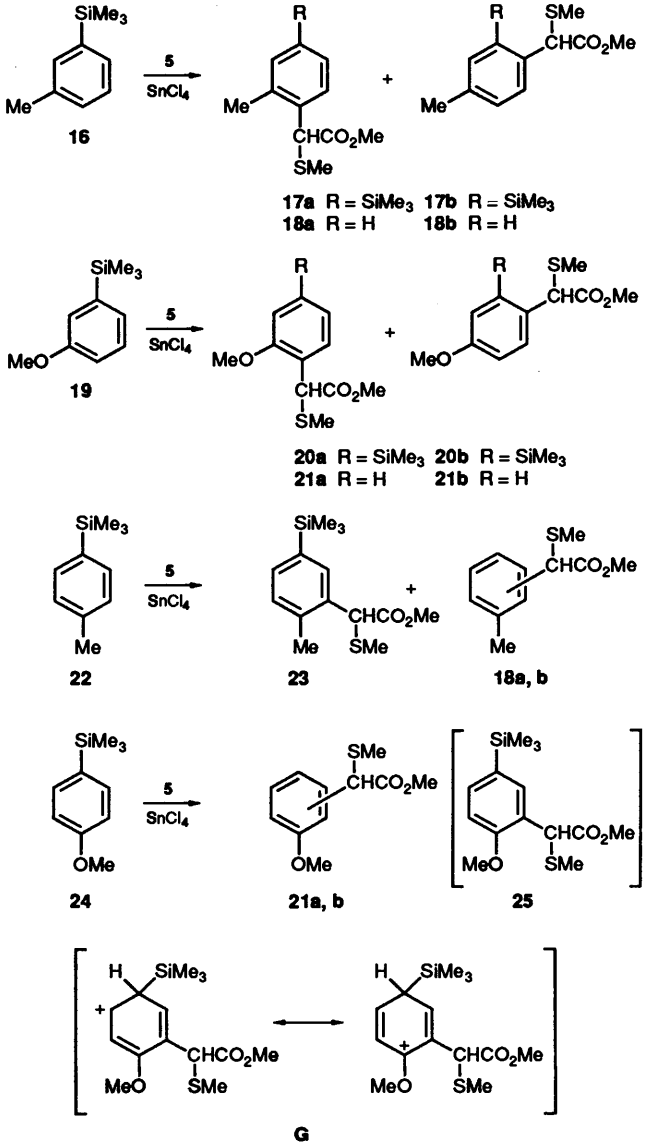
† A preliminary study showed that the correlation of these results with Hammett σ^+ values is very poor; both the *m*-TMS and *p*-TMS points deviate seriously from the linearity. It is desirable that these data should be re-examined to ascertain whether or not it constitutes a real deviation.

‡ It is of interest to note that the isomers substituted at the *ortho* position to the TMS group dominate by 3:2 in both cases. This result seems to indicate that the steric bulkiness exerted by the TMS group to the *ortho*-attack is comparable to or somewhat smaller than that of the methyl or methoxy group. Apparently the long carbon–silicon bond (189 pm) is responsible for this.

Table 1 Competitive Friedel–Crafts alkylation of trimethylphenylsilane **4** with the α-chlorosulfide **5** in the presence of tin(IV) chloride in dichloromethane solution at 20 °C

		Isomer distribution (%)			Partial rate factors		
Ar	$k_{Ar}/k_{benzene}$	*ortho*	*meta*	*para*	f_{o-}	f_{m-}	f_{p-}
Benzene	1.00						
Trimethylphenylsilane	3.81	4.6	65.8	30.0	0.53	7.53	6.87
Toluene	152.4[a]	11.7	0.3	88.0	52.4	1.5	804

[a] Since it was difficult to obtain accurate results for competitive alkylation with benzene, this value was calculated from $k_{(phenylsilane)}/k_{(toluene)} = 0.025$.



Scheme 4

by a GLC analysis) and the desilylated products **18a, b** (7%). The structures of **17a** and **17b** were confirmed by protodesilylation to **18a, b**, respectively. Since the ratio (16:84) of the minor products **18a, b** is essentially identical with that (*ortho*:*para* = 12:88) obtained from the reaction of toluene itself with **5**, it seems reasonable to assume that **18a, b** arise by attack of **5** on toluene formed *via* protodesilylation of **16** by hydrogen chloride generated during the reaction.

(*m*-Methoxyphenyl)trimethylsilane **19**, when treated with the α-chlorosulfide **5**, gave a mixture of the alkylated products **20a, b** in 77% yield in a ratio of 39:61.* The structures of **20a, b** were assigned again by conversion to the desilylated compounds **21a, b**.

Upon treatment with the α-chlorosulfide **5**, trimethyl-*p*-tolylsilane **22** gave the alkylated product **23** (57%) and the desilylated products **18a, b** (9%, 14:86). The structure of **23** was confirmed by protodesilylation to **18a**. The reaction of *p*-methoxyphenyltrimethylsilane **24** with **5** was found to give a mixture of the desilylated products **21a, b** in 77% yield (71:29). Taking account of the *ortho*/*para* ratio (33:67) for the products of the Friedel–Crafts reaction of anisole with **5**, it would appear that the main pathway for the formation of the *ortho*-isomer of **21a** involves the initial Friedel–Crafts alkylation of **24** followed by protodesilylation of the resulting **25**, whereas the *para*-isomer of **21b** arises largely by initial protodesilylation of **24** followed by Friedel–Crafts alkylation of resulting anisole. Protodesilylation of **25** is facilitated because the σ-complex intermediate **G** is stabilised by both silyl and methoxy groups.[18]

In summary, the present study revealed that the TMS group in the Friedel–Crafts alkylation is a slightly activating substituent on the benzene ring but shows essentially no directing effect.

Experimental

IR spectra were recorded with a JASCO A-100 spectrophotometer. ^{1}H NMR spectra were determined with a JEOL JNM-PMX 60 (60 MHz) or a Varian XL-300 (300 MHz), for solutions in $CDCl_3$. δ-Values quoted are relative to tetramethylsilane and *J* values are given in Hz. Exact mass (MS) determinations were obtained on an Hitachi M-80 instrument at 20 eV. GLC was carried out on a Shimadzu GC-14A gas chromatograph (helium carrier gas; capillary column at 220 °C). Column chromatography was performed on silica gel 60 PF_{254} (Merck) under pressure.

Friedel–Crafts Reaction of Trimethylphenylsilane **4** *with Methyl Chloro(methylthio)acetate* **5**. *General Procedure*.—To a solution of **4** (2.26 g, 15 mmol) and **5** (0.78 g, 3 mmol) in dichloromethane (20 cm^3) was added tin(IV) chloride (0.78 g, 3 mmol) at room temperature, and the mixture was stirred for 30 min. Water (10 cm^3) was added and the organic layer was separated off, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel with hexane–ethyl acetate (10:1) to give unchanged **4** and an inseparable mixture of the three regioisomers of *methyl* 2-(*methylthio*)-2-(*trimethylsilylphenyl*)*acetates* **6** (0.43 g, 54%) as an oil (Found: C, 57.8; H, 7.6. $C_{13}H_{20}O_2SSi$ requires C, 58.2; H, 7.5%); $\nu_{max}(CCl_4)$/cm^{-1} 1745 and 1250; δ_H(60 MHz) 0.23, 0.40 (total 9 H, both s, $SiMe_3$), 2.10 (3 H, s, SMe), 3.73 (3 H, s, OMe), 4.50 (1 H, s, SCH) and 7.16–7.6 (4 H, m, ArH).

The isomer ratio of **6** was found to be *ortho*:*meta*:*para* = 4:67:29 by a GLC analysis.

* See footnote ‡ on p. 1954.

Desulfurisation of **6**.—A mixture of **6** (0.23 g, 0.85 mmol) and Raney nickel (*ca.* 200 mg) in ethanol (10 cm^3) was refluxed for 1 h. The catalyst was filtered off, and the filtrate was concentrated. The residue was chromatographed on silica gel with hexane–ethyl acetate (10:1) to give methyl 2-(trimethylsilylphenyl)acetates **7** (0.17 g, 90%) as an inseparable mixture which was found to consist of the *ortho*-, *meta*- and *para*-isomers in a ratio of 4:68:28 by GLC analysis. Each peak was identified by a direct comparison with that of respective authentic sample (*vide infra*).

General Procedure for the Preparation of Methyl 2-[2-, 3- *and* 4-(*Trimethylsilyl*)*phenyl*]*acetates* **7**.—A solution of (trimethylsilylphenyl)acetic acids (0.10 g, 0.48 mmol), prepared according to the reported procedures[9] from the corresponding halogenotoluenes, in diethyl ether (2 cm^3) was added to an ethereal solution containing excess amounts of diazomethane at 0 °C. After nitrogen gas evolution ceased, the solvent was evaporated off. The residue was chromatographed on silica gel with hexane–ethyl acetate (10:1) to give the methyl ester. The following methyl esters were prepared.

The *ortho*-isomer of **7** (Found: $M^+ - 1$, 221.0957. $C_{12}H_{17}O_2Si$ requires $M - 1$, 221.0996); $\nu_{max}(CCl_4)/cm^{-1}$ 1745 and 1250; δ_H(60 MHz) 0.32 (9 H, s, $SiMe_3$), 3.68 (3 H, s, OMe), 3.76 (2 H, s, CH_2CO) and 7.13–7.6 (4 H, m, ArH); an oil.

The *meta*-isomer of **7** (Found: M^+ 222.1079. $C_{12}H_{18}O_2Si$ requires M, 222.1075); $\nu_{max}(CCl_4)/cm^{-1}$ 1745 and 1250; δ_H(60 MHz) 0.25 (9 H, s, $SiMe_3$), 3.62 (3 H, s, OMe), 3.68 (2 H, s, CH_2CO) and 7.16–7.46 (4 H, m, ArH); an oil.

The *para*-isomer of **7**;[9c] $\nu_{max}(CCl_4)/cm^{-1}$ 1745 and 1250; δ_H(60 MHz) 0.25 (9 H, s, $SiMe_3$), 3.60 (3 H, s, OMe), 3.66 (2 H, s, CH_2CO) and 7.22, 7.45 (2 H each, AB q, J 8, ArH).

Protodesilylation of **6**.—A solution of **6** (100 mg) in carbon tetrachloride (10 cm^3) containing trifluoroacetic acid (2 cm^3) was refluxed for 10 h. The solvent was evaporated off and the residue was chromatographed on silica gel with hexane–ethyl acetate (10:1) to give a colourless oil of methyl 2-methylthio-2-phenylacetate **8**[19] (62 mg, 85%), which was identical with an authentic sample in all respects. No desilylation took place at room temperature.

Friedel–Crafts Reaction of Trimethylphenylsilane **4** *with Ethyl* (*Chloromethylthio*)*acetate* **9**.—To a solution of **4** (1.34 g, 8.90 mmol) and **9** (0.50 g, 2.97 mmol) in dichloromethane (20 cm^3) was added tin(IV) chloride (0.77 g, 2.97 mmol) and the mixture was stirred at room temperature for 7 h. Water (10 cm^3) was added to the reaction mixture and the whole was extracted with dichloromethane. The extract was dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel with hexane–ethyl acetate (10:1). The first fraction gave the unchanged **4** and the second fraction gave *ethyl* [(trimethylsilylphenyl)methylthio]acetates 10 (0.34 g, 41%) as on oily mixture of *ortho*:*meta*:*para* = 3:71:26 (determined by GLC) (Found: C, 59.55; H, 8.0. $C_{14}H_{22}O_2SSi$ requires C, 59.5; H, 7.85%); $\nu_{max}(CCl_4)/cm^{-1}$ 1735 and 1250; δ_H(60 MHz) 0.26, 0.35 (total 9 H, both s, $SiMe_3$), 1.28 (3 H, t, J 8, CH_2CH_3), 3.06, 3.20 (total 2 H, both s, SCH_2CO), 3.83 (2 H, br s, $ArSCH_2$), 4.18 (2 H, q, J 8, CH_2CH_3) and 7.23–7.60 (4 H, m, ArH). The third fraction gave compound **11**[10] (0.13 g, 20%) as an oil.

Desulfurisation of **10**.—Using a procedure similar to that described for the preparation of **7**, **10** (0.165 g, 0.58 mmol) was desulfurized with Raney nickel to give trimethyltolylsilanes **12** as a mixture of *ortho*:*meta*:*para* = 8:58:34. These peaks were identified with each authentic sample prepared from the respective chlorotoluenes according to the reported procedure.[9]

Friedel–Crafts Reaction of 1,3-*Bis*(*trimethylsilyl*)*benzene* **13** *with* **5**.—Following the general procedure; **13** (1.62 g, 10 mmol) was treated with **5** (0.31 g, 2 mmol) in dichloromethane (20 cm^3) in the presence of tin(IV) chloride (0.52 g, 2 mmol) for 30 min at room temperature. The crude products were chromatographed on silica gel with hexane–ethyl acetate (1:1) to give unchanged **13** and an inseparable oily mixture of **14** and **15** (0.31 g, 55%) in a ratio of *ca.* 90:10 (Found: C, 56.25; H, 8.5. $C_{16}H_{28}O_2SSi_2$ requires C, 56.4; H, 8.3%); $\nu_{max}(CCl_4)/cm^{-1}$ 1745 and 1250; δ_H(300 MHz) 0.27 (18 H, s, $SiMe_3$ × 2), 2.12 (3 H, s, SMe), 3.75 (3 H, s, OMe), 4.53 (1 H, s, CH), 7.56 (2 H, d, J 2.0, ArH) and 7.60 (1 H, t, J 2.0, ArH).

Competitive Alkylation of Trimethylphenylsilane **4** *and Benzene*.—To a solution of **4** (1.503 g, 10.0 mmol), benzene (0.781 g, 10.0 mmol), and the α-chlorosulfide **5** (0.309 g, 2.0 mmol) in dichloromethane (30 cm^3) was added tin(IV) chloride (0.521 g, 2.0 mmol) and the mixture was stirred at 20 °C for 5 min and the whole was extracted with dichloromethane. The extract was dried ($MgSO_4$) and concentrated to give an oily residue (1.739 g). The relative amounts of the products were determined by a GLC analysis using naphthalene as internal standard. The results are as follows: **8**: 11.97 × 10^{-3} mmol; the *ortho*-isomer of **6**: 2.08 × 10^{-3} mmol (4.61%); the *meta*-isomer of **6**: 29.98 × 10^{-3} mmol (65.8%); the *para*-isomer of **6**: 13.48 × 10^{-3} mmol (30.0%). The relative reactivity of the phenylsilane **4** and benzene was calculated by the equation of Ingold *et al.*,[20] where the subscripts i and f signify initial and final. Partial rate factors were calculated according to the following equations;

$$k(\text{phenylsilane})/k(\text{benzene}) = (\log_{10}[PhSiMe_3]_i - \log_{10}[PhSiMe_3]_f)/(\log_{10}[PhH]_i - \log_{10}[PhH]_f) = 3.81$$

$$f_{o-} = k(\text{phenylsilane})/k(\text{benzene}) \times 6/2 \times (\%ortho\text{-isomer})/100 = 0.53$$

$$f_{m-} = k(\text{phenylsilane})/k(\text{benzene}) \times 6/2 \times (\%meta\text{-isomer})/100 = 7.53$$

$$f_{p-} = k(\text{phenylsilane})/k(\text{benzene}) \times 6/1 \times (\%para\text{-isomer})/100 = 6.87$$

Competitive Alkylation of the Phenylsilane **4** *and Toluene*.—The phenylsilane **4** (13.527 g, 90 mmol) and toluene (0.276 g, 3 mmol) in dichloromethane (50 cm^3) was treated with **5** (0.309 g, 2 mmol) in the presence of tin(IV) chloride (0.521 g, 2.0 mmol) at 20 °C for 5 min. It was then worked up, analysed, and calculated as described above; k(phenylsilane)/k(toluene) = 0.025.

Friedel–Crafts Reaction of Trimethyl(3-*methylphenyl*)*silane* **16** *with* **5**.—Following the general procedure; **16** (1.64 g, 10 mmol) was treated with **5** (0.31 g, 2.0 mmol) in the presence of tin(IV) chloride (0.52 g, 2.0 mmol). After work-up, the crude material was chromatographed on silica gel with hexane–ethyl acetate (10:1). The first fraction gave unchanged **16** and the second fraction gave *methyl* 2-[4-*methyl*-2-(*trimethylsilyl*)-*phenyl*]-2-(*methylthio*)*acetate* **17b** (0.21 g, 36%) as an oil (Found: M^+, 282.1092. $C_{14}H_{22}O_2SSi$ requires M, 282.1108); $\nu_{max}(CCl_4)/cm^{-1}$ 1750 and 1250; δ_H(60 MHz) 0.39 (9 H, s, $SiMe_3$), 2.15 (3 H, s, SMe), 2.33 (3 H, s, ArMe), 3.72 (3 H, s, CO_2Me), 4.75 (1 H, s, SCH), 7.04–7.3 (2 H, m, ArH) and 7.56 (1 H, d, J 8, ArH). The third fraction gave *methyl* 2-[2-*methyl*-4-(*trimethylsilyl*)*phenyl*]-2-(*methylthio*)*acetate* **17a** (0.215 g, 36%) as an oil (Found: M^+, 282.1092); $\nu_{max}(CCl_4)/cm^{-1}$ 1750 and 1250; δ_H(60 MHz) 0.26 (9 H, s, SiMe), 2.08 (3 H, s, SMe), 2.41 (3 H, s, ArMe), 3.70 (3 H, s, CO_2Me), 4.72 (1 H, s, SCH) and

7.20–7.63 (3 H, m, ArH). The fourth fraction gave **18a, b** (0.028 g, 7%, 16:84).

Protodesilylation of **17a**.—A solution of **17a** (92 mg, 0.33 mmol) in carbon tetrachloride (10 cm^3) containing trifluoroacetic acid (2 cm^3) was stirred at room temperature overnight. The solvent was evaporated off, and the residue was chromatographed on silica gel with hexane–ethyl acetate (10:1) to give **18a** (68 mg, 100%) as an oil.

Photodesilylation of **17b**.—Using the above procedure, **17b** (27 mg, 0.096 mmol) was treated with trifluoroacetic acid to give **18b** (14 mg, 76%) as an oil.

Friedel–Crafts Reaction of (3-Methoxyphenyl)trimethylsilane **19** *with* **5**.—Following the general procedure; **19** (1.80 g, 10 mmol) was treated with **5** (0.31 g, 2.0 mmol) in the presence of tin(IV) chloride (0.52 g, 2.0 mmol). After work-up, the residue was chromatographed on silica gel with hexane–ethyl acetate (10:1) to give an inseparable mixture of *methyl 2-(2-methoxy-4-trimethylsilylphenyl)-2-(methylthio)acetate* **20a** and *methyl 2-(4-methoxy-2-trimethylsilylphenyl)-2-(methylthio)acetate* **20b** (0.46 g, 77%) in a ratio of 39:61 as an oil (Found: M^+ 298.1057. $C_{14}H_{22}O_3SSi$ requires *M*, 298.1057); $\nu_{max}(CCl_4)/cm^{-1}$ 1745 and 1245; δ_H(60 MHz) 0.20, 0.32 (total 9 H, both s, $SiMe_3$), 2.07 (3 H, s, SMe), 3.66 (3 H, s, CO_2Me), 3.75, 3.80 (total 3 H, both s, ArOMe), 4.66, 4.90 (total 1 H, both s, SCH) and 6.7–7.63 (3 H, m, ArH).

Protodesilylation of **20a, b**.—Using a procedure similar to that described for the preparation of **18a**, the mixture of **20a, b** (100 mg, 0.34 mmol) was treated with trifluoroacetic acid (2 cm^3) to give a mixture of **21a, b**[13] (57 mg, 76%) (Found: C, 58.3; H, 6.3. Calc. for $C_{11}H_{14}O_3S$: C, 58.4; H, 6.2%); $\nu_{max}(CCl_4)/cm^{-1}$ 1745; δ_H(60 MHz) 2.07, 2.13 (total 3 H, both s, SMe), 3.73 (3 H, s, CO_2Me), 3.80, 3.87 (total 3 H, both s, ArOMe), 4.50, 4.98 (total 1 H, both s, SCH) and 6.78–7.62 (4 H, m, ArH).

Friedel–Crafts Reaction of Trimethyl(4-methylphenyl)silane **22** *with* **5**.—Following the general procedure; **22** (1.64 g, 10 mmol) was treated with **5** (0.31 g, 2.0 mmol) in the presence of tin(IV) chloride (0.52 g, 2.0 mmol). After work-up, the residue was chromatographed on silica gel with hexane–ethyl acetate (10:1). The first fraction gave unchanged **22** and the second fraction gave *methyl 2-(2-methyl-5-trimethylsilylphenyl)-2-(methylthio)acetate* **23** (0.34 g, 57%) as an oil (Found: M^+, 282.1083. $C_{14}H_{22}O_2SSi$ requires *M*, 282.1108); $\nu_{max}(CCl_4)/cm^{-1}$ 1750 and 1250; δ_H(60 MHz) 0.25 (9 H, s, $SiMe_3$), 2.10 (3 H, s, SMe), 2.38 (3 H, s, ArMe), 3.71 (3 H, s, CO_2Me), 4.73 (1 H, s, SCH), 7.10, 7.35 (1 H, each, AB q, *J* 8, ArH) and 7.59 (1 H, s, ArH). The third fraction gave a mixture of **18a** and **18b** (0.040 g, 9%) in a ratio of 14:86 as an oil.

Protodesilylation of **23**.—Using a procedure similar to that described for the preparation of **18a** from **17a**, **23** (29 mg, 0.10 mmol) was treated with trifluoroacetic acid (0.5 cm^3) to give **18a** (18 mg, 78%).

Friedel–Crafts Reaction of (4-Methoxyphenyl)trimethylsilane **24** *with* **5**.—Following the general procedure, **24** (1.80 g, 10 mmol) was treated with **5** (0.31 g, 2.0 mmol) in the presence of tin(IV) chloride (0.52 g, 2.0 mmol). After work-up, the residue was chromatographed on silica gel with hexane–ethyl acetate (5:1). The first fraction gave **24** and the second fraction gave an inseparable mixture of **21a, b** (0.365 g, 77%) in a ratio of 71:29 as an oil.

Acknowledgements

The authors thank associate professor Tadashi Okuyama, Osaka University, for valuable suggestions and discussions, and Misses Haruko Nakamura, Satoko Morita and Sumiyo Mitani for technical assistance.

References

1 E. W. Colvin, *Silicon in Organic Synthesis*, Butterworth, London, 1981, p. 125.
2 W. P. Weber, *Silicon Reagents for Organic Synthesis*, Springer-Verlag, Berlin, 1983, p. 114.
3 I. Fleming, *Comprehensive Organic Chemistry*, eds. D. H. R. Barton and W. D. Ollis, Pergamon Press, Oxford, 1979, vol. 3, p. 613.
4 R. A. Benkeser and P. E. Brumfield, *J. Am. Chem. Soc.*, 1951, **73**, 4770; J. L. Speier, *J. Am. Chem. Soc.*, 1953, **75**, 2930; T. Hashimoto, *Yakugaku Zasshi*, 1967, **87**, 524.
5 B. Lepeška and V. Chvalovský, *Collect. Czech. Chem. Commun.*, 1969, **34**, 3553.
6 R. Calas and J. Gerval, *C.R. Hebd. Seances Acad. Sci. Ser. 2*, 1987, **305**, 1423.
7 For reviews in this field, see Y. Tamura and H. Ishibashi, *Yuki Gosei Kagaku Kyokai Shi*, 1982, **40**, 658; H. Ishibashi and M. Ikeda, *Yuki Gosei Kagaku Kyokai Shi*, 1989, **47**, 330; H. Ishibashi, *Yakugaku Zasshi*, 1989, **109**, 685.
8 Part of this work appeared in a preliminary communication: H. Ishibashi, H. Sakashita, S. Morita, S. Mitani and M. Ikeda, *Chem. Lett.*, 1989, 603.
9 (*a*) R. G. Severson, R. J. Rosscup, D. R. Lindberg and R. D. Engberg, *J. Am. Chem. Soc.*, 1957, **79**, 6540; (*b*) M. Frankel, M. Broze, D. Gertner, A. Rotman, A. Shenhar and A. Zilkha, *J. Med. Chem.*, 1968, **11**, 857; (*c*) A. J. Cornish and C. Eaborn, *J. Chem. Soc., Perkin Trans. 2*, 1975, 874; (*d*) M. C. Sleevi and J. F. Wolfe, *J. Org. Chem.*, 1980, **45**, 5204.
10 Y. Tamura, T. Tsugoshi, H. Annoura and H. Ishibashi, *Synthesis*, 1984, 326; Y. Tamura, H. Annoura, M. Fuji, M. Okura and H. Ishibashi, *Chem. Pharm. Bull.*, 1986, **34**, 540.
11 H. C. Brown and B. A. Bolto, *J. Am. Chem. Soc.*, 1959, **81**, 3320.
12 D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, 1952, **74**, 6246; G. Baddeley, G. Holt and D. Voss, *J. Chem. Soc.*, 1952, 100; H. C. Brown and H. Jungk, *J. Am. Chem. Soc.*, 1955, **77**, 5579; R. H. Allen and L. D. Yats, *J. Am. Chem. Soc.*, 1959, **81**, 5289. For other examples, see G. A. Olah, *Friedel–Crafts and Related Reactions*, ed. G. A. Olah, Interscience Publishers, New York, 1963, vol. 1, p. 68; D. A. McCaulay, *Friedel–Crafts and Related Reactions*, ed. G. A. Olah, Intersciences Publishers, New York, 1964, vol. 2, p. 1061.
13 Y. Tamura, H.-D. Choi, H. Shindo and H. Ishibashi, *Chem. Pharm. Bull.*, 1982, **30**, 915; Y. Tamura, H.-D. Choi, M. Mizutani, Y. Ueda and H. Ishibashi, *Chem. Pharm. Bull.*, 1982, **30**, 3574.
14 R. L. Hillard III and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, 1977, **99**, 4058.
15 M. E. Freeburger and L. Spialter, *J. Am. Chem. Soc.*, 1971, **93**, 1894; C. Eaborn, D. R. M. Walton and R. D. Topsom, *J. Organomet. Chem.*, 1972, **43**, 131; W. Adcock, G. L. Aldous and W. Kitching, *Tetrahedron Lett.*, 1978, 3387 and refs. therein.
16 F. A. Carey and R. J. Sundberg, *Advanced Organic Chemistry*, Plenum Press, New York, 1984, 2nd edn., p. 497.
17 P. Sykes, *A Guidebook to Mechanism in Organic Chemistry*, Longman, London, 1981, 5th edn., p. 155.
18 C. Eaborn and P. M. Jackson, *J. Chem. Soc., B*, 1969, 21; F. P. Bailey and R. Taylor, *J. Chem. Soc., B*, 1971, 1446.
19 W. Reeve and C. W. Woods, *J. Am. Chem. Soc.*, 1960, **82**, 4062; K. Nishihata and M. Nishio, *Tetrahedron Lett.*, 1976, 1695.
20 C. K. Ingold and M. S. Smith, *J. Chem. Soc.*, 1938, 905; C. K. Ingold, A. Lapworth, E. Rothstein and D. Ward, *J. Chem. Soc.*, 1931, 1959.

Paper 2/015881
Received 25*th March* 1992
Accepted 11*th May* 1992