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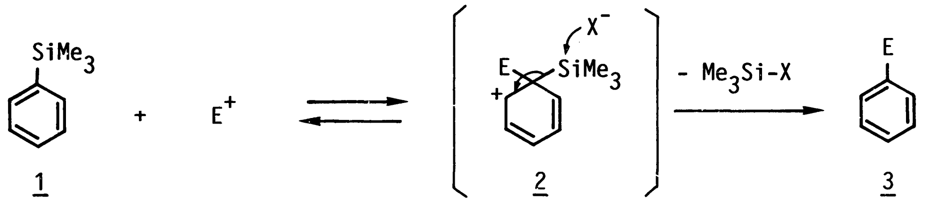
Friedel-Crafts Alkylation of Phenylsilanes with α-Chloro Sulfides

Hiroyuki ISHIBASHI,* Hiroshi SAKASHITA, Satoko MORITA, Sumiyo MITANI,
and Masazumi IKEDA
Kyoto Pharmaceutical University, Misasagi, Yamashina, Kyoto 607

Treatment of trimethylphenylsilane with methyl chloro(methylthio)acetate in the presence of atannic chloride gave a mixture of the alkylated silylbenzenes, in which the *meta*- and *para*-substituted products predominated. The partial rate factors of this reaction suggest that the trimethylsilyl group slightly activates the *meta*- and *para*-positions of the silylbenzene.

The reactions of arylsilanes, *e.g.* **1**, with electrophiles (H^+, I^+, NO_2^+ *etc*.,) occur, in general, at the ring carbon carrying the silyl group to give the *ipso*-substitution products **3**.1,2) Friedel-Crafts alkylation is not exceptional. For examples, in the presence of aluminum chloride, trimethylphenylsilane reacts with benzyl bromide to give diphenylmethane,3) and the reaction of 1,2-*bis*(trimethylsilyl)benzene with *t*-butyl chloride gives (2-*t*-butylphenyl)trimethylsilane.4) These *ipso*-substitution reactions are formulated as proceeding *via* delocalized cationic intermediates **2** stabilized by the β-carbon-silicon bond.

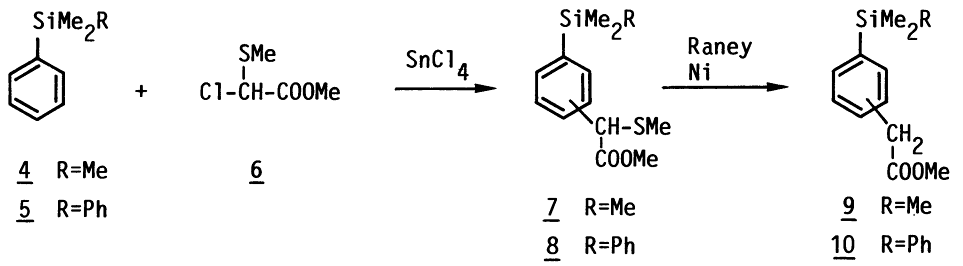


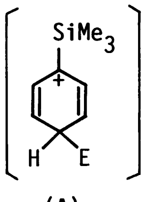
Here we report a hitherto unknown normal (deprotonative) Friedel-Crafts alkylation of phenylsilanes, which gives rise to *meta*- and *para*-substituted phenylsilanes as the major products instead of *ipso*-substituted products. The effects of the substituents upon orientation in this reaction are also described.

Thus, when trimethylphenylsilane (**4**)(15 mmol) was treated with methyl chloro-(methylthio)acetate (**6**)(3 mmol) in the presence of stannic chloride (3 mmol) in methylene dichloride (20 ml) at room temperature for 30 min, the alkylated products **7** were obtained in 54% yield (based on the chloro sulfide **6**) as a mixture of three regioisomers in a ratio of *o*:*m*:*p*=4:67:29 (determined by GLC). No *ipso*-substitution product was detected in the reaction mixture.

Similar treatment of dimethyldiphenylsilane (**5**) with the α-chloro sulfide **6** afforded a mixture of the alkylated products **8** in 43% yield (*m*:*p*=72:28).

The structure of the mixtures **7** and **8** was established by a GLC comparison of the corresponding desulfurized mixtures **9** and **10** with respective authentic samples prepared from *o*-, *m*-, and *p*-halotoluenes.$^{5)}$





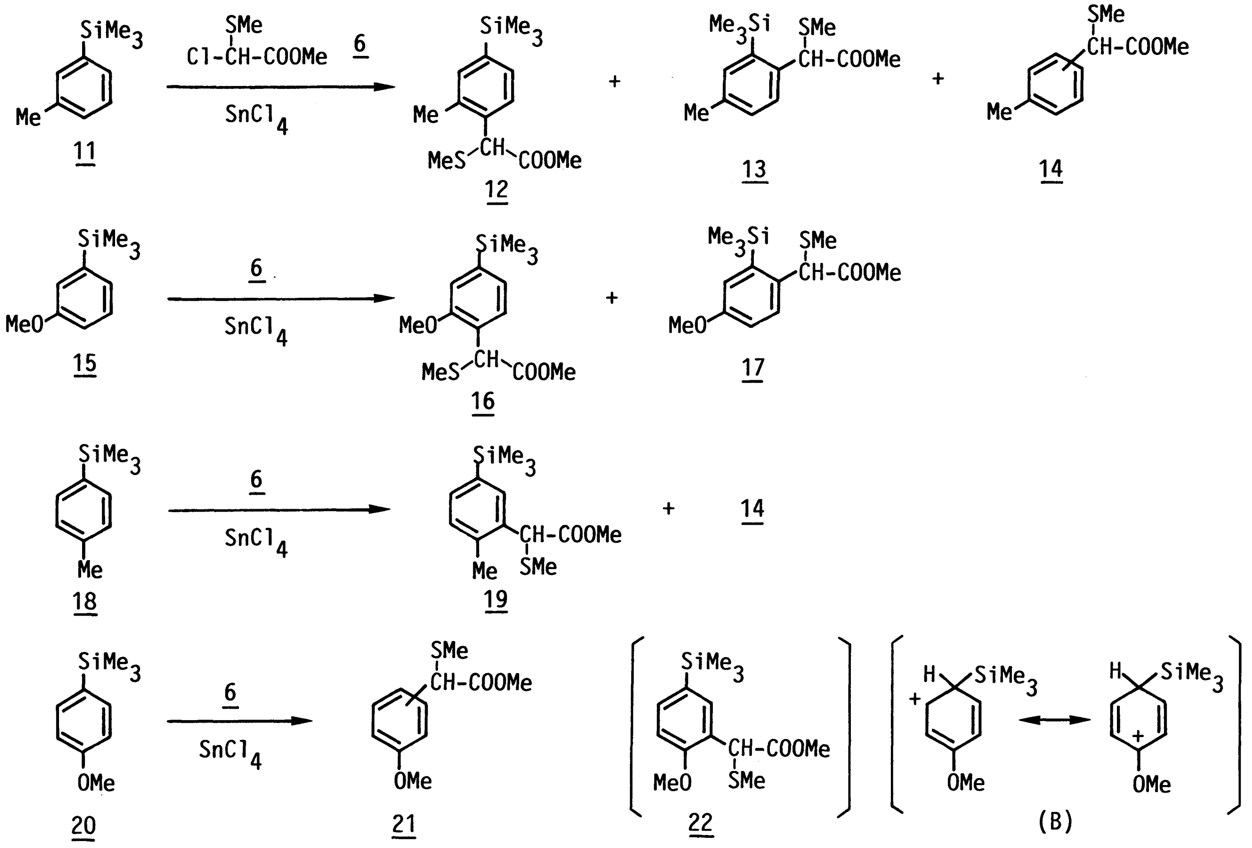
(A)

The partial rate factors of trimethylphenylsilane (**4**) for the reaction with the α-chloro sulfide **6** were estimated to be $f_{o-}=0.5$, $f_{m-}=7.5$, and $f_{p-}=6.7$ (based on benzene=1), indicating that the trimethylsilyl group slightly activates both the *meta*- and *para*-positions in the phenyl ring, compared with benzene. This result would be a reflection of a weak elecron-donating inductive effect of the trimethylsilyl (TMS) group. However, this stabilizing effect seems to be not large enough to stabilize selectively the transition state (or intermediate) (A) leading to the *para*-substituted products,$^{6,7)}$ as shown by essentially the same f_{m-} and f_{p-} values.

The lack of the *ipso*-substitution product may be attributed to the steric repulsion between the TMS group and the bulky Friedel-Crafts complex $[Cl_4\overset{\delta-}{Sn}\cdots Cl\text{-}\overset{\delta+}{C}H(SMe)COOMe]$ formed from the α-chloro sulfide and a Lewis acid.$^{8)}$

We were then led to see the effects of substituents upon orientation in this reaction, in order to evaluate the directive effect of the TMS group. Thus, reaction of trimethyl-*m*-tolylsilane (**11**) with the α-chloro sulfide **6** gave **12**(36%),$^{9)}$ **13**(36%)$^{9)}$ (the product ratio of **12**:**13**=41:59, determined by GLC), and the desilylated products **14**(7%, *o*:*p*=16:84). Since the *ortho*/*para* ratio of the reaction products **14** is essentially the same as that (12:88) obtained from the reaction of toluene itself with **6**, it is reasonable to assume that **14** arises by attack of **6** on toluene formed *via* protodesilylation of **11** by hydrogen chloride generated during the reaction. Reaction of (*m*-methoxyphenyl)trimethylsilane (**15**) with the α-chloro sulfide **6** gave a mixture of the alkylated products **16**$^{9)}$ and **17**$^{9)}$ in 77% yield in a ratio of 39:61. In contrast to the case of **11**, no desilylated products were detected, presumably because the methoxy derivative **15** is so reactive that protodesilylation cannot compete with the Friedel-Crafts reaction. It is interesting to note that the isomer substituted at the *ortho* position to the TMS group was formed as the major products in both the cases. This result seems to indicate that the steric effect exerted by the TMS group to the *ortho* attack is somewhat smaller than that of the methyl or methoxy group.

Upon treating with the α-chloro sulfide **6**, trimethyl-*p*-tolylsilane (**18**) gave the alkylated product **19**$^{9)}$ (57%) and the desilylated products **14**(9%, *o*:*p*=14:86), while *p*-methoxyphenyltrimethylsilane (**20**) gave a mixture of the desilylated



products **21** in 77% yield (*o*:*p*=71:29). Taking account of the result that the *ortho*/*para* ratio for the products of the Friedel-Crafts reaction of anisole with **6** is 33:67, it would appear that the formation of the *ortho*-isomer of **21** involves the initial Friedel-Crafts alkylation of **20** followed by protodesilylation of the resulting **22**, whereas the *para*-isomer of **21** the initial protodesilylation of **20** followed by Friedel-Crafts alkylation of resulting anisole. Protodesilylation is facilitated in **20** because the σ-complex intermediate (B) is stabilized by both silyl and methoxy groups.[10] In the reactions of these substituted phenylsilanes, methyl or methoxy group determines the position that the substitution takes place.

References

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2) Only the exception is a nitration of trimethylphenylsilane with copper nitrate or with 90% fuming nitric acid in acetic anhydride to give the nitrated phenylsilanes along with the nitro-desilylated compound (nitrobenzene): see R.A. Benkeser and P.E. Brumfield, J. Am. Chem. Soc., **73**, 4770 (1951); T. Hashimoto, Yakugaku Zasshi, **87**, 524 (1967).

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4) C. Eaborn, D.R.M. Walton, and D.J. Young, J. Chem. Soc., B, 1969, 15.

5) R.G. Severson, R.J. Rosscup, D.R. Lindberg, and R.D. Engberg, J. Am. Chem. Soc., 79, 6540 (1957); M. Frankel, M. Broze, D. Gertner, A. Rotman, A. Shenhar, and A. Zilkha, J. Med. Chem., 11, 857 (1968); A.J. Cornish and C. Eaborn, J. Chem. Soc., Perkin Trans. 2, 1975, 874; M.C. Sleevi and J.F. Wolfe, J. Org. Chem., 45, 5204 (1980).

6) It has been reported that an α-silyl group is less effective in stabilizing tertiary carbenium ions than an α-methyl group, but is more stabilizing than hydrogen: see Y. Apeloig and A. Stanger, J. Am. Chem. Soc., 107, 2806 (1985).

7) It should be pointed out that an argument that the transition state (or intermediate) for *meta*-attack is stabilized by the TMS group β to carbenium ion center 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.

8) The reactive species of the reaction with *t*-butyl chloride might be a *t*-butyl cation.

9) The structures of **12**, **13**, **16**, **17**, and **19** were confirmed by a comparison of the corresponding desilylated compounds or mixture with authentic samples prepared by a Friedel-Crafts reaction of toluene or anisole with the α-chloro sulfide **6**. Protodesilylation was carried out by treating the silylated compounds in trifluoroacetic acid at room temperature overnight.

10) C. Eabon and P.M. Jackson, J. Chem. Soc., B, 1969, 21; F.P. Bailey and R. Taylor, ibid., 1971, 1446.

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