



A new highly sterically demanding silyl (TEDAMS) group. Synthesis by multiple substitution of tris(diphenylmethyl)silane with diarylcarbenium ions

Kimitada Terao, Takashi Watanabe, Takafumi Suehiro, Toshiki Nokami, Jun-ichi Yoshida *

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Nishikyō-ku, Kyoto 615-8510, Japan

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ABSTRACT

A highly efficient electrochemical method for synthesis of halosilanes bearing bulky substituents was developed. Electrophilic multiple substitution on tris(diphenylmethyl)silane with diarylcarbenium ions afforded a highly sterically demanding hydrosilane, tris(extended diarylmethyl)silane (TEDAMS-H), which was converted to the corresponding bromosilane (TEDAMS-Br).

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Silyl groups bearing extremely bulky substituents have received significant research interest from a view point of sterically demanding substituents.^{1–4} For example, extensive studies have been made on the chemistry of trityldimethylsilyl (TrDMS) group,^{5–7} tris(trimethylsilyl)-silyl (TTMSS or supersilyl) group, which contains UV labile Si–Si bond,^{8–12} bowl-shaped tris(2,6-diphenylbenzyl)silyl (TDS) group^{13,14} and tris(2,2'',6,6''-tetramethyl-*m*-terphenyl-5'-yl)silyl (TRMS) group¹⁵ (Fig. 1). We report herein the synthesis of a new highly sterically demanding silyl (tris(extended diarylmethyl)silyl, TEDAMS) group based on multiple substitution of tris(diarylmethyl)silane with diarylcarbenium ions.

The present works stem from our earlier work¹⁶ on the construction of dendritic molecules using the cation pool method.^{17–26} During the course of our study, we realized that a CH₂SiR₃ group is an excellent activating group of a phenyl group²⁷ toward the electrophilic substitution with diarylcarbenium ions.^{28,29} Thus, we envisioned that organosilanes bearing multiple diphenylmethyl groups serve as effective cores for construction of sterically demanding silyl groups by electrophilic multiple substitution with diarylcarbenium ions (Fig. 2).^{30,31}

Conventionally, bulky silyl groups are synthesized by nucleophilic substitution on silicon using the corresponding organomagnesium¹³ or organolithium¹⁵ reagents. This method requires multisteps such as preparation of bulky organometal reagents and manipulation of a latent halogen substituent on a silicon atom. The present method serves as an alternative approach, which may

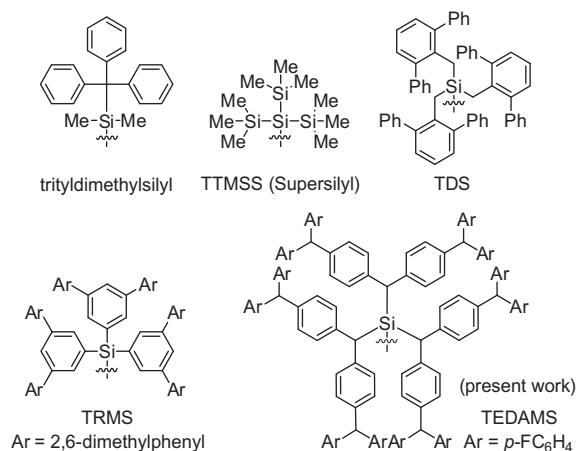


Figure 1. Sterically demanding silyl groups.

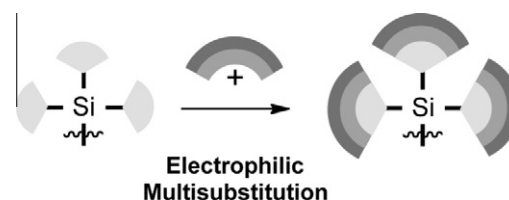


Figure 2. Strategies for the synthesis of TEDAMS group.

* Corresponding author. Tel.: +81 75 383 2726; fax: +81 75 383 2725.

E-mail address: yoshida@sbchem.kyoto-u.ac.jp (J. Yoshida).

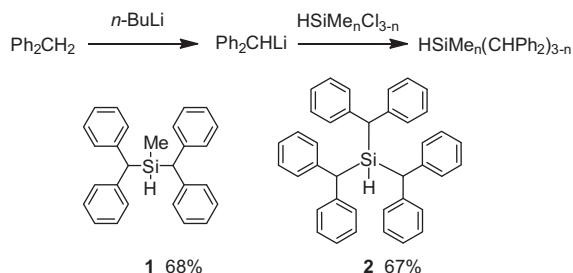


Figure 3. Preparation of hydrosilanes equipped with several diphenylmethyl groups.

expand the scope of the chemistry of sterically demanding silyl groups.

We initiated our work by preparing organosilicon compounds which have multiple diphenylmethyl groups (Fig. 3). These organosilicon compounds were prepared by the reaction of diphenylmethyl lithium with corresponding chlorosilanes. Bis(diphenylmethyl)methylsilane **1** and tris(diphenylmethyl)silane **2** were obtained in 68% and 67% yields, respectively.

Next, we examined electrophilic multisubstitution of bis(diphenylmethyl)methylsilane **1** with diarylcarbenium ion **4**, which was prepared from di(*p*-fluorodiphenyl)methane **3** (8 equiv) by the low-temperature electrochemical oxidation based on the 'cation pool' method (Fig. 4).^{32,33} The tetrasubstituted product **5** was obtained in 41% yield, in which hydride was converted to fluoride. In this case, both the substitution on the phenyl groups and the fluorination occurred. Presumably, the hydride was abstracted by the diarylcarbenium ion followed by the fluorination with tetrafluoroborate counter anion (BF_4^-).³⁴ In fact, it is known that triphenylcarbenium perchlorate can abstract the hydride from hydrosilanes.^{35–37}

However, no fluorination was observed for the reaction of tris(diphenylmethyl)silane **2** with diarylcarbenium ion **4** (Fig. 5). The corresponding hexasubstituted hydrosilane **6** was obtained in 67% yield. This is probably because of higher steric hindrance around the silicon atom in **2** than that in **1**.

Finally, we investigated the conversion of hydrosilane **6** to the corresponding bromosilane **7**, which may be more useful for the introduction of TEDAMS group (Fig. 6). It was reported that tris(2,6-diphenylbenzyl)silane (TDS-H) was converted to the corresponding bowl-shaped bromosilane quantitatively by the reaction with Br_2 in 1 h at -78°C .¹³ Hydrosilane **6** was recovered when it was treated with Br_2 at -78°C , indicating that hydride in **6** is more sterically hindered than TDS-H. However, the corresponding

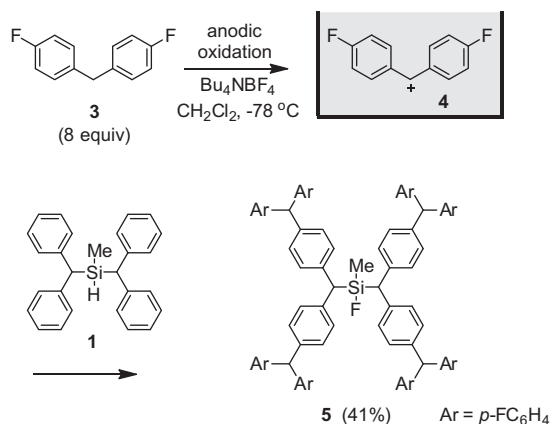


Figure 4. Electrophilic multisubstitution of hydrosilane **1** with diarylcarbenium ion **4**.

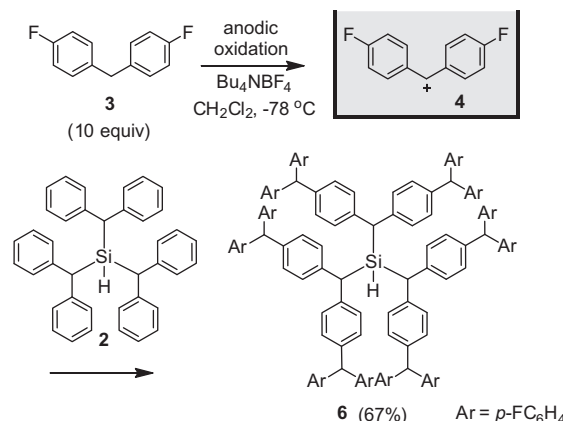


Figure 5. Electrophilic multisubstitution of hydrosilane **2** with diarylcarbenium ion **4**.

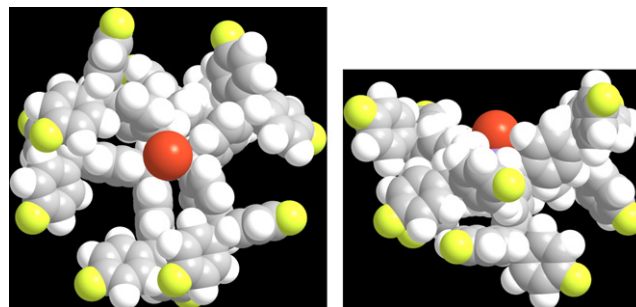
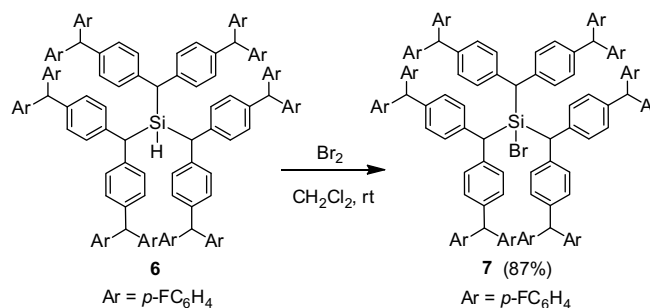


Figure 6. Conversion of hydrosilane **6** to bromosilane **7**. H (white), C (gray), Si (purple), F (light green), Br (red) are shown in each colors.^{38,39}

bromosilane **7** was obtained in 87% when the reaction was carried out at room temperature. Bromosilane **7** has reasonable stability and can be handled in open air, indicating that the bromosilane moiety is kinetically stabilized by bulky dendritic substituents. As observed in the computationally optimized structure of bromosilane **7**, steric hindrance of substituents is significant (see [Supplementary data](#) for details).

In summary, we have developed an efficient method for the construction of a highly sterically demanding silyl (TEDAMS) group using multiple substitution on the phenyl groups of tris(diphenylmethyl)silane with diarylcarbenium ions generated by the 'cation pool' method. Further optimization of the present method and applications of this highly sterically demanding silyl group are under investigation in our laboratory.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.05.140.

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