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Double Silylation of Olefin with $HSiCl_3$ in the Presence of Bu_4PCl. New Synthetic Method for α,*β*-Bis(trichlorosilyl)alkanes

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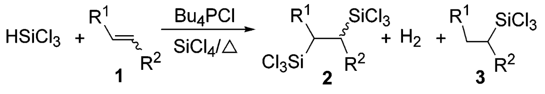
*Summary: Terminal and activated internal olefins such as 1-hexene, 1-decene, styrene, p-methylstyrene, 1-phenylprop-l-ene, and stilbene reacted with a mixture of $HSiCl_3$ and $SiCl_4$ in the presence of Bu_4PCl at 180 °C for 4−16 h to give the α,β-bis(trichlorosilyl)alkanes **2** (70−85%) and alkyltrichlorosilanes **3** (10−21%). However, the reactions of the unactivated internal olefins 3-hexene and cyclopentene for 32 h under the same conditions gave 41% and 85% consumption and produced the bis-silylation compounds **2** in 12 and 43% yields along with hydrosilylation products **3** in 24 and 28% yields, respectively.*

Trichlorosilane ($HSiCl_3$) undergoes a variety of interesting and useful Si−C bond formation reactions with organometallic reagents[1] and unsaturated organic compounds in the presence of transition-metal complexes[2] to give various organosilanes containing Si−Cl bonds as functionalities, which are used as important starting materials in the silicones industry.[3] Another established Si−C bond forming method is the organic base catalyzed reaction of $HSiCl_3$ with activated organic compounds such as alkyl chlorides[4] and unsaturated hydrocarbons.[5] Tertiary amines catalyze the coupling reaction of activated organic chlorides[4] with $HSiCl_3$ and the hydrosilylation of olefins,[5] affording alkyltrichlorosilanes in good and relatively low yields, respectively. Recently, we have reported successful coupling reactions with organic chlorides affording alkyltrichlorosilanes in high yields in the presence of quaternary phosphonium chloride as an organic salt catalyst in place of amine[6,7] and the introduction of $SiCl_2$ to butadienes to form 1,1-dichlorosilacyclopent-3-enes in good yields.[8] The success of these coupling reactions prompted us to extend the reaction strategy to olefins, which are widely used as monomers in the plastics industry.[9] When an activated styrene (**1a**) as a representative olefin reacted with 4 equiv of $HSiCl_3$ in the presence of 10 mol % Bu_4PCl at 180 °C for 4 h, surprisingly, the double-silylation products α,*β*-bis(trichlorosilyl)ethylbenzene (**2a**)[5,10] and a mixture of two isomeric [(dichlorosilyl)(trichlorosilyl)ethyl]benzenes (**2a′**) were obtained as the major products in 77 and 9% GLC yields, respectively. In addition to these bis-silylation compounds, a product of hydrosilylation, **3a**, which was obtained as a major product in the amine-catalyzed reaction of **1a**,[5] was formed in 11% yield. When the same reaction was carried out using a mixture of 4 equiv of $HSiCl_3$ and 4 equiv of $SiCl_4$,[11] **2a** was formed in up to 85% yield while compounds **2a′** almost disappeared. In this reaction, the same number of moles of hydrogen gas evolved as moles of **2a** that were produced. The reaction works effectively with a variety of olefins. In this paper, we wish to communicate a new and facile synthetic method for α,*β*-bis(trichlorosilyl)alkanes through the double silylation of a variety of olefins with a mixture of $HSiCl_3$ and $SiCl_4$ in the presence of Bu_4PCl (eq 1). The results obtained from the coupling of olefins are given in Table 1. To simplify the Si−C bond forming reactions and to favor the formation of **2**, excess amounts of $HSiCl_3$ and $SiCl_4$ as a coreactant were used.



(1)

As shown in Table 1, the reactions of **1a**−**h** with the mixture of $HSiCl_3$ and $SiCl_4$ gave two types of silylation compounds, the α,*β*-bis-silylation compounds **2** and the hydrosilylation compounds **3**. Compounds **2** and **3** could be easily purified by fractional distillation under vacuum, respectively**.** Terminal olefins **1a**−**d** afforded **2a**−**d** (72−85%) as the major products and **3a**−**d** (10−21%). Activated olefins **1a**,**b** were almost consumed within 4 h to give **2a**,**b** in 85% and 83% yields, respectively (entries 1 and 2). Unactivated olefins **1c**,**d** required

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(11) General procedure for synthesis of **2**: as a representative example, the synthesis of **2a** is described as follows. A 25 mL dried bomb with a valve was charged with Bu_4PCl (0.28 g, 0.95 mmol), **1a** (1.00 g, 9.60 mmol), $HSiCl_3$ (5.20 g, 38.39 mmol), $SiCl_4$ (6.52 g, 38.38 mmol), and *n*-dodecane (1.0 mL) under a dry nitrogen atmosphere. The reaction was carried out at 180 °C for 4 h and gave **2a** and **3a** in 85 and 9% GLC yields, respectively, along with H_2 (ca. 197 mL at 20 °C). Compound **2a** (2.78 g, bp 110−112 °C/0.3 Torr) was obtained in 78% isolated yield by vacuum distillation from the reaction mixture.

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Table 1. Bu_4PCl-Catalyzed Coupling Reaction of Olefins 1 with a Mixture of $HSiCl_3$ and $SiCl_4$[a]

entry no.	reactant			reacn time (h)	products (%)[c]	
	1[b]	R^1	R^2		**2**	**3**
1	**a** (−)	Ph	H	4	85	10
2	**b** (−)	*p*-MePh	H	4	83	13
3	**c** (−)	*n*-butyl	H	16	75	21
4	**d** (14)	*n*-octyl	H	16	72	12
5	**e** (−)	Ph	trans-Me	12	83[d]	14[12]
6	**f** (6)	Ph	trans-Ph	12	70[e]	21[13]
7	**g** (59)	ethyl	trans-ethyl	32	12[f]	24
8	**h** (15)	cyclopentene		32	43[g]	28

[a] The reaction was carried out using a 40:40:10:1 mol ratio of $HSiCl_3$, $SiCl_4$, **1**, and Bu_4PCl at 180 °C. [b] Numbers in parentheses represent unreacted **1** (%) that remained. [c] Yields are based on the amount of **1** used and were determined by GLC with use of the internal standard. [d] A 3:2 mixture of two diastereomers. [e] A 3:1 mixture of two diastereomers. [f] A 15:1 mixture of two diastereomers. [g] A 1:1 mixture of *cis*- and *trans*-**2h**.

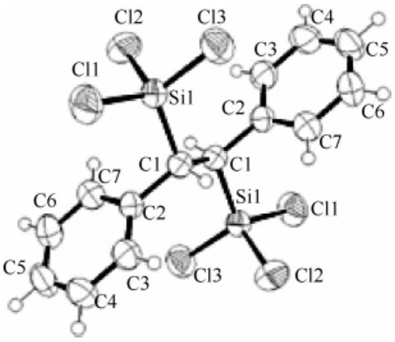
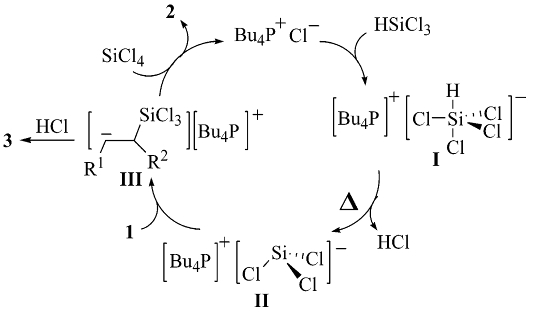


Figure 1. Single-crystal X-ray diffraction structure of (1*R*(*S*),2*S*(*R*))-**2** with thermal ellipsoids at the 50% probability level.

a longer reaction time and gave **2c**,**d** in 75 and 72% yields along with **3c**,**d** in 22 and 12% yields with 99% and 86% consumption of reactants after 16 h, respectively (entries 3 and 4). The reactions of internal olefins **1e**−**h** gave **2e**−**h**, each consisting of two diastereomers (D1 and D2). The reactions of activated **1e**,**f** under the same conditions proceeded more slowly than those for the activated terminal olefins **1a**,**b** and afforded **2e** (83%, D1:D2 = 3:2) and **2f** (70%, D1:D2 = 3:1) as major products along with **3e** (14%) and **3f** (21%) after 12 h, respectively (entries 5 and 6). However, the reactions of unactivated internal olefins, linear **1g** and cyclic **1h**, proceeded slowly and gave **2g** (12%, D1:D2 = 15:1) and **2h** (43%, cis: trans = 1:1) along with **3g** (24%) and **3h** (28%) with 41 and 85% consumption of reactants **1**, respectively, after the longer time of 32 h (entries 7 and 8). Unactivated internal alkenes could also be utilized in this bis-silylation reaction, although side products were more evident. These results show that general olefins undergo effectively the coupling reactions with $HSiCl_3$ in the presence of Bu_4PCl to give the bis-silylation compounds **2** as major products, except for the aliphatic internal alkene **1g**. In the characterization of compounds **2e**−**g**, each diastereomer from the mixtures of two diastereomers could not be purified by preparative GLC. Fortunately, one (D1) of the two diastereomers of **2f** could be isolated as a single crystal. The single-crystal structure was determined by X-ray diffraction to be (1*R*(*S*),2*S*(*R*))-**2f** in a staggered conformation with a carbon−carbon bond of length 1.55 Å with a torsion angle of 180° between both phenyl and both silyl groups, respectively (Figure 1).

Most significant is the facile synthesis of a variety of new α,*β*-bis(trichlorosilyl)alkanes with many Si−Cl functionalities, starting from commercially available olefins and $HSiCl_3$. Even though it was reported that some bis-silylation compounds resulted from double silylation of simple olefins using special alkylsilanes with two silicon atoms such as bis(dimethylsilyl)-benzene[14] and alkyldisilanes[15] in the presence of transition-metal complexes, the syntheses of such α,*β*-bis(trichlorosilyl)alkanes were previously unavailable by simple means.

Scheme 1. Proposed Mechanism for the Formation of 2



On the basis of our results, we propose a mechanism for the Bu_4PCl-catalyzed reaction of **1** with $HSiCl_3$ as shown in Scheme 1. Bu_4PCl interacts with $HSiCl_3$ to form the pentacoordinated intermediate **I**,[5,16] which loses hydrogen chloride upon heating to give the silyl anion intermediate **II**. The intermediate **II** adds to the carbon−carbon double bond of **1** to form the carbanion intermediate **III**. The intermediate **III** can react with $SiCl_4$ to give the bis-silylation product **2**. Hydrogen chloride formed from the intermediate **I** reacts with the intermediate **III** to give the hydrosilylation product **3** and with excess hydrosilanes to afford dihydrogen and chlorosilanes in competition. It appears that the last reaction occurs predominantly under our conditions, except for the reaction of **1g**, which gives the bis-silylation compounds **2**, and self-polymerization of olefins does not occur. It is well-known that general olefins are readily polymerized both by heat and in the presence of cationic reagents.[17] The reaction preference of olefins **1** for bis-silylation is attributed to the stabilities of the intermediates **III**.

In conclusion, we describe a new and facile synthetic approach to α,*β*-(trichlorosilyl)alkanes bearing six chlorine substituents on the two silicon atoms, which may provide starting materials for the preparation of new silicones. The extension of this reaction to other specific olefins and alkynes is currently being investigated.

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Supporting Information Available: Text, tables and figures giving experimental procedures, characterization data for all new compounds, and ^1H and ^{13}C NMR spectra for compounds **2a**−**h** and a CIF file giving crystallographic data for (1*R*(*S*),2*S*(*R*))-**2f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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