Friedel−Crafts Alkylation of Polychlorobenzenes with (1,2-Dichloroethyl)trichlorosilane

Joon Soo Han,† Weon Cheol Lim,† Bok Ryul Yoo,† Jung-Il Jin,‡ and Il Nam Jung*,†

Organosilicon Chemistry Laboratory, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, Korea, and Department of Chemistry, Korea University, 1-Anam-dong, Seoul 130-701, Korea

Received April 16, 2002

(1,2-Dichloroethyl)trichlorosilane (**2**) reacted with a 6-fold excess of mono-, di-, and trichlorobenzenes at 120 °C in the presence of aluminum chloride to give regiospecific (2,2-diarylethyl)trichlorosilanes via a carbocation rearrangement. The yields were 61−69%, and regioisomers of (1,2-diarylethyl)silanes were not obtained. Alkylation of 1,2,3,4-tetrachlorobenzene with **2** did not give [2,2-bis(tetrachlorophenyl)ethyl]trichlorosilane or 9,10-bis(silyl)methyl-9,10-dihydroanthracenes but gave cyclic silyl-substituted indanes in 84% yield via the acid-catalyzed dimerization of *β*-(trichlorosilyl)styrene formed by the first alkylation, followed by dehydrochlorination. The structure of 1,2-*trans*-2,3-*trans*-4,5,6,7-tetrachloro-1-(2,3,4,5-tetrachlorophenyl)-2-(trichlorosilyl)-3-((trichlorosilyl)methyl)indane has been determined by X-ray crystallography. The desilylated product, 1,3-*cis*-4,5,6,7-tetrachloro-1-(2,3,4,5-tetrachlorophenyl)-3-((trichlorosilyl)methyl)indane, was reduced by $LiAlH_4$, and its structure was also determined.

Introduction

Friedel−Crafts alkylations with organic compounds such as organic halides, alkenes, and alkynes in the presence of Lewis acid catalysts have been extensively studied for many years and are well-established routes for introducing alkyl substituents onto aromatic rings.[1] In contrast, alkylations using silicon compounds were first reported by Wagner et al. in 1953, for the preparation of (phenylethyl)trichlorosilane.[2] In the following year, Petrov reported the Friedel−Crafts alkylation of benzene derivatives with (chloroalkyl)silanes.[3] Since then, only a few articles on alkylation using alkenylchlorosilanes[4] and (chloroalkyl)silanes[5] have been published.

Recently we reported the Friedel−Crafts alkylation of aromatic compounds with allylchlorosilanes,[6] vinylchlorosilanes,[7] and (chlorinated alkyl)silanes[8] to give (2-arylpropyl)-, (2-arylethyl)-, and (phenylalkyl)chlorosilanes, respectively, under mild conditions. We also studied the one-step Friedel−Crafts-type cycloalkylation of biphenyl using (dichloroalkyl)chlorosilanes, which gave in moderate yields the cyclized products, fluorenes substituted at the 9-carbon with (chlorosilyl)alkyl groups.[12] Lewis acid catalyzed Friedel−Crafts alkylations have now become one of the most powerful methods for incorporating aromatic substituents into organochlorosilanes.[9]

Although the alkylation of polyhalogenated benzenes such as trichlorobenzene[10] and polyfluorinated benzenes[11] with polychlorinated methanes has been reported to give alkylation products, the yields were low due to the deactivation effects of the electron-withdraw-

† Korea Institute of Science and Technology.
‡ Korea University.

(1) (a) Roberts, R. M.; Khalaf, A. A. *Friedel−Crafts Alkylation Chemistry*; Marcel Dekker: New York, 1984. (b) Olah, G. A. In *Friedel−Crafts and Related Reactions*; Wiley-Interscience: New York, London, Sydney, 1963; Vols. I−IV, and references therein.

(2) Wager, G. H.; Bailey, D. L.; Pines, A. N.; Dunham, M. L.; McIntire, D. B. *Ind., & Eng. Chem.* **1953**, *45*, 367.

(3) Petrov, A. D.; Mironov, V. F.; Ponomarenko, V. A.; Chernyshev, E. A. *Dokl. Akad. Nauk SSSR* **1954**, *97*, 687; *Chem. Abstr.* **1955**, *51*, 10166g.

(4) (a) Andrianov, K. A.; Zhdanov, A. A.; Odinnets, V. A. *Zh. Obshch. Khim.* **1961**, *31*, 4033; *Chem. Abstr.* **1962**, *57*, 9874a. (b) Andrianov, K. A.; Zhdanov, A. A.; Odinnets, V. A. *Zh. Obshch. Khim.* **1962**, *32*, 1126; *Chem. Abstr.* **1963**, *58*, 1484a. (c) Nametkin, N. S.; Vdovin, V. M.; Findel-Shtein, E. S.; Oppengeim, V. D.; Chekalina, N. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1966**, *11*, 1998. (d) Voronkov, M. G.; Kovrigin, V. M.; Lavrent'ev, V. I.; Moralev, V. M. *Dokl. Akad. Nauk SSSR* **1985**, *281*(6), 1374.

(5) (a) Petrov, A. D.; Chernyshev, E. A.; Dolgaya, M. E. *Zh. Obshch. Khim.* **1955**, *25*, 2469; *Chem. Abstr.* **1956**, *50*, 9319a. (b) Chernyshev, E. A.; Dolgaya, M. E. *Zh. Obshch. Khim.* **1957**, *27*, 48; *Chem. Abstr.* **1957**, *51*, 12045g. (c) Chernyshev, E. A.; Dolgaya, M. E.; Egorov, Yu. P. *Zh. Obshch. Khim.* **1957**, *27*, 267; *Chem. Abstr.* **1958**, *52*, 7187b. (d) Chernyshev, E. A.; Dolgaya, M. E.; Egorov, Y. P.; Semenov, L. V.; Petrov, A. D. *Zh. Obshch. Khim.* **1958**, *28*, 613; *Chem. Abstr.* **1958**, *52*, 17150b. (e) Chernyshev, E. A.; Dolgaya, M. E.; Egorov, Yu. P. *Zh. Obshch. Khim.* **1958**, *28*, 2829; *Chem. Abstr.* **1959**, *53*, 9110c. (f) Chernyshev, E. A.; Dolgaya, M. E. *Zh. Obshch. Khim.* **1959**, *29*, 1850; *Chem. Abstr.* **1960**, *54*, 8604d. (g) Cer, L.; Vaisarova, V.; Chvaiovsky, V. *Collect. Czech. Chem. Commun.* **1967**, *32*, 3784; *Chem. Abstr.* **1968**, *68*, 21992u.

(6) (a) Lee, B. W.; Yoo, B. R.; Kim, S.-I.; Jung, I. N. *Organometallics* **1994**, *13*, 1312. (b) Ahn, S.; Song, Y.-S.; Yoo, B. R.; Jung, I. N. *Organometallics* **2000**, *19*, 2777.

(7) (a) Cho, E. J.; Lee, V.; Yoo, B. R.; Sohn, H.; Powell, D. R.; West, R.; Jung. I. N. *Organometallics* **1997**, *16*, 4200. (b) Cho, E. J.; Lee, V.; Yoo, B. R.; Jung, I. N. *J. Organomet. Chem.* **1997**, *548*, 237.

(8) (a) Yoo, B. R.; Kim, J. H.; Lee, H.-J.; Lee, K.-B.; Jung, I. N. *J. Organomet. Chem.* **2000**, *605*, 239. (b) Yoo, B. R.; Kim, J. H.; Cho, B. G.; Jung, I. N. *J. Organomet. Chem.* **2001**, *631*, 36.

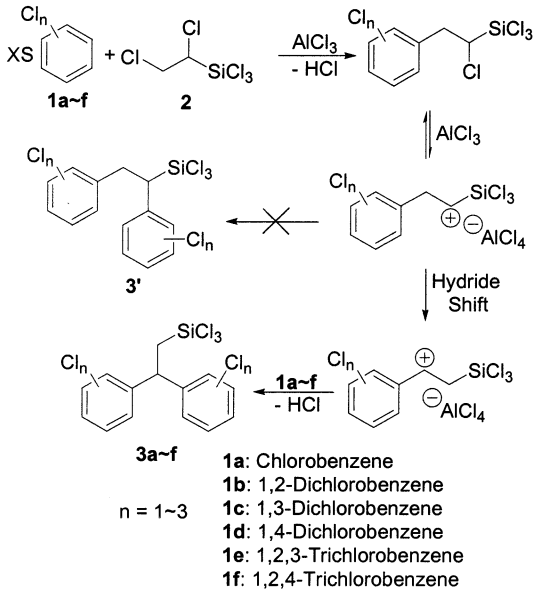
(9) Jung, I. N.; Yoo, B. R. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 2001; Vol. 46, p 145.

(10) (a) Wilson, S. D.; Huang, H.-Y., *J. Chin. Chem. Soc.* **1936**, *4*, 142. (b) Mendelson, W. L.; Spainhour, C. B.; Jones, S. S.; Lam, B. L.; Wert, K. L. *Tetrahedron Lett.* **1980**, *21*, 1393.

(11) Beckert, W. F.; Lowe, J. U., Jr. *J. Org. Chem.* **1967**, *32*, 582.

10.1021/om020296c CCC: $22.00
Publication on Web 08/06/2002

Scheme 1



ing halogen substituents. To the best of our knowledge, the analogous alkylations of polychlorinated benzenes with organosilanes have never been reported. Encouraged by our success in cycloalkylation using dichloroalkylsilicon compounds,[12] we attempted the alkylation and cyclization of polychlorinated benzenes with (1,2-dichloroethyl)trichlorosilane (**2**). The reactions of mono-, di-, and trichlorobenzenes proceeded to give alkylation products, [2,2-bis(chlorophenyl)ethyl]trichlorosilanes, while tetrachlorobenzene gave the cyclized silyl-substituted indanes but not [2,2-bis(tetrachlorophenyl)ethyl]-trichlorosilane or 9,10-bis(silyl)methyl-9,10-dihydroanthracenes. In this paper, we report our results in detail.

Results and Discussion

Alkylation of Chlorinated Benzenes with 2. Six chlorinated benzenes, chlorobenzene (**1a**), 1,2-dichlorobenzene (**1b**), 1,3-dichlorobenzene (**1c**), 1,4-dichlorobenzene (**1d**), 1,2,3-trichlorobenzene (**1e**), and 1,2,4-trichlorobenzene (**1f**), in 6-fold excess were alkylated with **2** in the presence of aluminum chloride as a catalyst to afford products **3a**−**f** (Scheme 1). We chose **2** as an alkylating agent because it can be easily prepared from the chlorination of vinyltrichlorosilane.[20] An excess of chlorinated benzenes **1a**−**f** was used to prevent polyalkylation on the same ring. The products could be easily isolated by vacuum distillation. The results obtained using optimized reaction conditions are summarized in Table 1.

Table 1. Alkylation Products of Chlorinated Benzenes 1a−f with 2[a]

reactant **1**	products **3** yield (%)[b]	no. of isomers	major isomer (portion (%))[c]
1a	**3a** (68)	6	[d] (37.1)
1b	**3b** (61)	3	bis(3,4-dichlorophenyl) (67.1)
1c	**3c** (63)	3	bis(2,4-dichlorophenyl) (86.6)
1d	**3d** (69)	1	bis(2,5-dichlorophenyl) (100)
1e	**3e** (65)	2	bis(2,4,5-trichlorophenyl) (91.9)
1f	**3f** (62)	3	bis(2,3,4-trichlorophenyl) (64.9)

[a] The mole ratio of **1** to **2** to $AlCl_3$ was 6:1:0.1, and all reactions were carried out at 120 °C for 20 min. [b] Isolated yield for a mixture of isomers. [c] The portion of the major isomer was determined by GLC area percent. [d] The major isomer could not be separated.

As shown in Table 1, the alkylation of **1a**−**f** with **2** at 120 °C for 20 min gave [2,2-bis(chlorophenyl)ethyl]-trichlorosilanes **3a**−**f** in good yields ranging from 61 to 69%, but the regioisomers [1,2-bis(chlorophenyl)ethyl]-trichlorosilanes were not obtained. The yields of alkylation products did not significantly decrease as the number of chlorine substituents on the ring increased, indicating that any deactivation effects of the chlorine substituents were overcome by the high reactivity of **2**.

Alkylation products **3a**−**f** consisted of mixtures from two to six isomers depending on the alkylation position on the benzene ring of **1**, except that of **3d** obtained from the symmetrical dichlorobenzene **1d**. The alkylation of **1a** with **2** gave an isomeric mixture of six [2,2-bis-(chlorophenyl)ethyl]trichlorosilanes (**3a**) in 68% yield without the [1,2-bis(chlorophenyl)ethyl]trichlorosilane regioisomers (**3a′**). These results are in contrast to the previous report on the alkylation of **1a** with **2** to give **3a′** in 27.4% yield.[5d] The formation of **3a** may be explained by first an alkylation at the carbon β to silicon, followed by a rearrangement of the resulting carbocation to the benzylic cation prior to the second alkylation. It has been also reported that the alkylation of benzene with 1,2-dichloropropane gave not only 1,2-diphenylpropane but also appreciable amounts of 1,1-diphenylpropane.[14] In our system, the stabilization effect of a benzylic cation and steric hindrance from the bulky trichlorosilyl group may be responsible for the regiospecific 2,2-diarylation products through cation rearrangement and hydride shifts. Because of the low reactivities of deactivated aromatic compounds, vigorous reaction conditions for the alkylation also make the cation rearrangement more favorable. Only traces of the reduction product, 2-(aryl)ethyltrichlorosilane, and polyalkylated products were detected by GC/MS analysis. In this series of reactions, tarry materials were also formed in small quantities, which lowered the yield of **3**. The products could be easily separated from the tar by vacuum distillation, but the polymeric tar was not analyzed.

Since the alkylation of **1a** with **2** takes place at the carbon which is ortho, meta, and para to Cl, the six isomers for compounds **3a** are possible due to the positions of chlorine on the two rings. Indeed, six isomers were detected using analytical GLC with relative intensities of 0.6:13.1:37.1:1.3:32.7:15.1 in the order of increasing retention time. According to GC-MS analysis data, six isomers of **3a** showed nearly the same

(12) Song, Y.-S.; Kong, S. D.; Khan, S. A.; Yoo, B. R.; Jung, I. N. *Organometallics* **2001**, *20*, 5586.
(13) Olah, G. A.; Flood, S. H.; Moffatt, M. E. *J. Am. Chem. Soc.* **1964**, *86*, 1065.
(14) Ransley, D. L. *J. Org. Chem.* **1966**, *31*, 3595.
(15) Angelbis, A.; Anschütz, R. *Chem. Ber.* **1884**, *17*, 165.
(16) Sisido, K.; Ishida, T. *J. Am. Chem. Soc.* **1948**, *70*, 1289.
(17) (a) Müller, A. *J. Org. Chem.* **1952**, *17*, 1077. (b) Rosen, M. J. *J. Org. Chem.* **1953**, *18*, 1701. (c) Corson, B. B.; Dorsky, J.; Nickels, J. E.; Kutz, W. M.; Thayer, H. I. *J. Org. Chem.* **1954**, *19*, 17. (d) Higashimura, T.; Hiza, M.; Hasegawa, H. *Macromolecules* **1979**, *12*, 1058. (e) Sawamoto, M.; Higashimura, T. *Macromolecules* **1981**, *14*, 467.
(18) (a) Brook, M. A.; Hülser, P.; Sebastian, T. *Macromolecules* **1989**, *22*, 3814. (b) Brook, M. A.; Sebstian, T.; Hülser, P.; Jüschke, R.; Wenzel, S.; Townsend, J. A.; Falletta, P. R. *Can. J. Chem.* **1995**, *73*, 1794.
(19) Müller, A.; Mészáros, M.; Karczag-Wilhems, A. *Chem. Ber.* **1954**, *87*, 1735.
(20) Agre, C. L.; Hilling, W. *J. Am. Chem. Soc.* **1952**, *74*, 3895.

fragmentation patterns and the molecular ion peaks appeared at *m*/*z* 382, 384, 386, 388, and 390 with relative intensities of 63:100:64:20:3, which match the isotope abundance ratio, 63:100:67:23:4, for the five chlorine atom containing species $C_{14}H_{11}Cl_5Si$. Similarly, the base peak corresponding to bis(chlorophenyl)methyl cation appeared at *m*/*z* 235, 237, and 239 with relative intensities of 10:6:1. These results indicate that the six components of the product mixture are the regioisomers due to the two chlorine atoms on the two phenyl rings. However, the individual isomers could not be separated and characterized separately due to their similar boiling points. The ring proton peaks in the NMR spectrum of the isomeric mixture were complex and could not be resolved. So far, they cannot be exactly characterized by other spectroscopic data.

In the case of the other polychlorobenzenes, three isomeric products were obtained from 1,2- and 1,3-dichlorobenzene, with the relative quantities of the products being 0.5:32.4:67.1 and 1.0:12.4:86.6, respectively. Three isomers with the relative intensities 7.5:27.6:64.9 were also obtained from 1,2,4-trichlorobenzene. Among these isomers, the major isomeric products were separated from the minor products by several consecutive recrystallizations from hexane solution. Their structures were determined by analyzing the ring proton peaks of the NMR spectra,[22] and their names are included in Table 1.

As shown in Table 1, the major isomer obtained from the alkylation of **1b** was [2,2-bis(3,4-dichlorophenyl)-ethyl]trichlorosilane. This result indicates that the ring carbon para to one chlorine and meta to the other is the most favorable position for the alkylation. The other two isomers may be less favorable because of the alkylation at the sterically hindered position ortho to chlorine. The major isomer obtained from the alkylation of **1c** was [2,2-bis(2,4-dichlorophenyl)ethyl]trichlorosilane, indicating that the chlorine substituents are ortho and para directors. The same ortho- and para-directing effect of chlorine was also observed in the alkylation of chlorobenzene with allylchlorosilanes.[6] Among the four available positions of **1c** for the alkylation, the carbon between two chlorine substituents should be less favorable due to the steric hindrance from both chlorines, and no alkylation product at that position was detected.

Among three possible isomers from the alkylation of **1e**, two products were obtained with a relative intensity of 8.1:91.9. This result demonstrates that the one position of **1e** is highly activated compared to the other position. Analysis of the isomers showed that [2,2-bis-(2,3,4-trichlorophenyl)ethyl]trichlorosilane was the major product. Therefore, the 4-position of **1e** seems to be the most favorable under our reaction conditions. This is also consistent with the fact that the chlorine substituents are ortho and para directors as observed above. The major isomer out of three isomers obtained from the alkylation of **1f** was [2,2-bis(2,4,5-trichlorophenyl)-ethyl]trichlorosilane. In this case, the alkylation did not occur at the carbon between two chlorines.

Alkylation of 1,2,3,4-Tetrachlorobenzene (1g) with 2. We attempted to alkylate and cyclize **1g** with **2** to prepare 9,10-bis((chlorosilyl)methyl)anthracene. Since all the electrophilic substitution sites for alkylation except two adjacent carbons of the ring are blocked by chlorine substituents, cycloalkylation should be more favorable than polyalkylation. The formation of 9,10-dimethyl-9,10-dihydroanthracene from the alkylation of benzene with 1,1-dichloroethane was claimed in the literature as early as 1884.[15] However, Sisido and co-workers reinvestigated the same reaction in 1948 and found that the product was actually 9,10-dimethylanthracene, resulting from the dehydrogenation and aromatization of 9,10-dimethyl-9,10-dihydroanthracene catalyzed by aluminum chloride.[16]

Although various reaction conditions were applied, 9,-10-bis((chlorosilyl)methyl)anthracene was not obtained from **1g**. Instead, silyl-substituted indanes, *rac*-1,2-*trans*-2,3-*trans*-4,5,6,7-tetrachloro-1-(2,3,4,5-tetrachlorophenyl)-2-(trichlorosilyl)-3-((trichlorosilyl)methyl)indane (**4**) and *rac*-1,3-*cis*-4,5,6,7-tetrachloro-1-(2,3,4,5-tetrachlorophenyl)-3-((trichlorosilyl)methyl)indane (**5**), were obtained (Scheme 2).

Since compounds **4** and **5** have the same mass numbers as the 9,10-dihydroanthracene-type product and its desilylated product, mass spectroscopic analysis was not helpful for the identification of the products. However, the NMR peaks were rather complex, and the analysis did not match the corresponding anthracene products. The two products were separated and purified by repeated recrystallization from hexane solution. The molecular structure of **4** was determined by X-ray crystallography, and the ORTEP plot of **4** is shown in Figure 1. Compound **4** was reacted with methylmagnesium chloride in THF to afford 1,2-*trans*-2,3-*trans*-4,5,6,7-tetrachloro-1-(2,3,4,5-tetrachlorophenyl)-2-(trimethylsilyl)-3-((trimethylsilyl)methyl)indane (**6**) in 66% yield. The structure of this methylated compound **6** is also shown in Figure 2. Since we were unable to obtain a single crystal of **5**, it was reduced with $LiAlH_4$ to afford the crystalline compound **7**. The structure of **7** was determined and is shown in Figure 3.

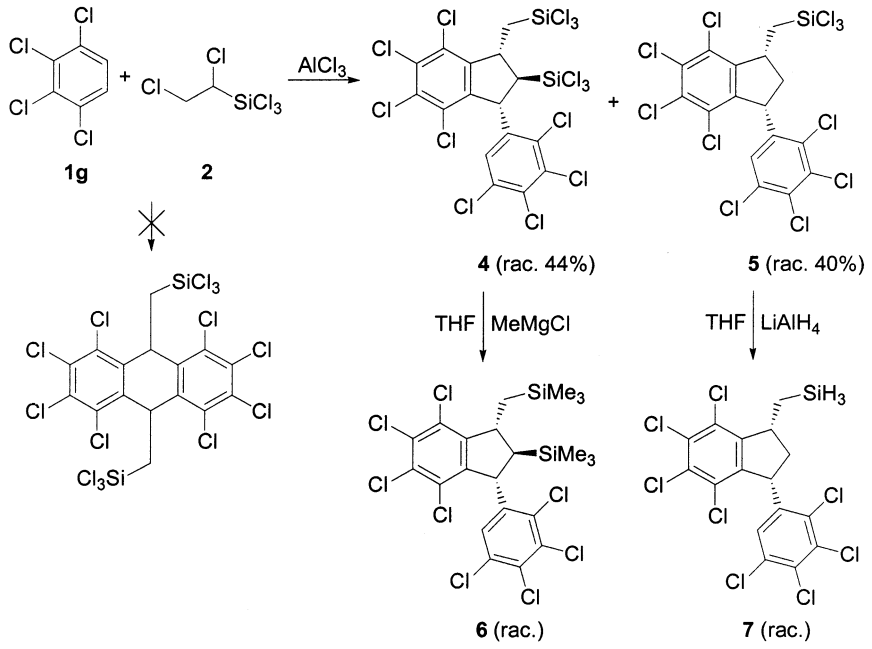
It is well-known that styrene is dimerized to 1-methyl-3-phenylindane in the presence of an acid catalyst.[17] Recently, Brook and co-workers reported that β-(trichlorosilyl)styrene dimerized in the presence of triflic acid to give 2-(trichlorosilyl)-1-((trichlorosilyl)methyl)-3-phenylindane.[18] On the basis of the formation of indane-type products, it may be concluded that tetrachlorinated β-trichlorosilylstyrene (**I**) was formed during the alkylation reaction. The formation of the intermediate **I** can be explained by the alkylation of tetrachlorobenzene with **2** to give (2-aryl-1-chloroethyl)trichlorosilane, followed by dehydrochlorination.

A possible mechanism for the formation of **4** and **5** is proposed in Scheme 3. Protonation of **I** would give a stable benzylic carbocation. It is also possible to form a carbocation directly from the first alkylation product, followed by dechlorination. This carbocation then rearranges to the more stable benzylic carbocation. Addition of **I** to the benzylic carbocation would be more favorable than addition to the sterically bulky **1g**. Ring closure by intramolecular alkylation gives the cyclic compound **4**. High reaction temperatures and the presence of

(21) Sheldrick, G. M. SHELX-97, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.

(22) Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. *Tables of Spectral Data for Structure Determination of Organic Compounds, Eng. Ed.*; Springer-Verlag: Berlin, 1983.

Scheme 2



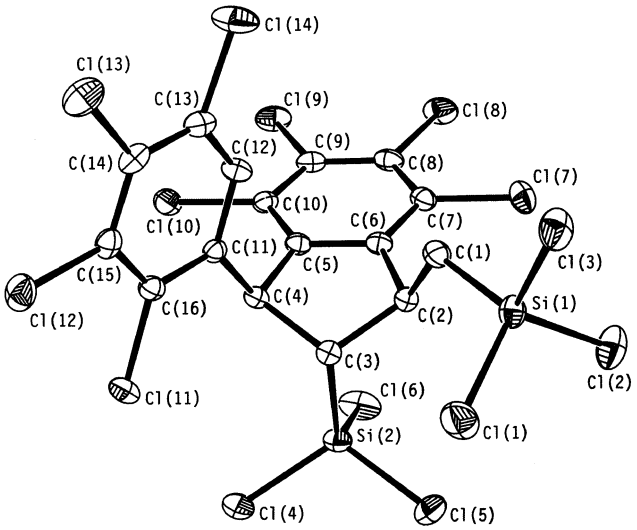


Figure 1. Molecular structure of (1*R*,2*S*,3*R*)-**4** (ellipsoids represent 30% probability level; hydrogen atoms are omitted for clarity). Only one enantiomer of the racemic mixture is shown.

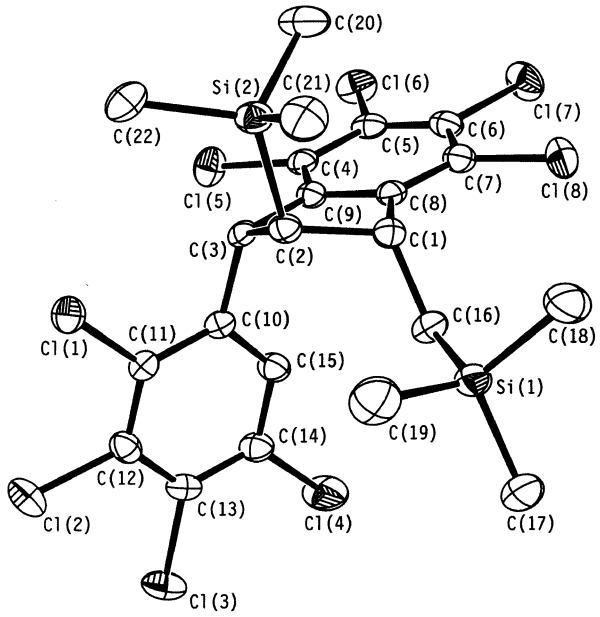


Figure 2. Molecular structure of (1*S*,2*R*,3*S*)-**6** (ellipsoids represent 30% probability level; hydrogen atoms are omitted for clarity). Only one enantiomer of the racemic mixture is shown.

hydrogen chloride promote desilylation to give the intermediate **II** followed by cycloalkylation, which would give compound **5**. Direct protiodesilylation from **4** to **5** is also possible.[6b] To check this possibility, HCl gas was bubbled into the mixture of **4** and **5** at 120 °C in the presence of $AlCl_3$. The amount of **5** was indeed increased, indicating that protiodesilylation occurred.

During the dimerization studies of *β*-(trichlorosilyl)-styrene in the presence of triflic acid, two isomeric products, 1,2-*cis*-2,3-*trans*-2-trichlorosilyl-1-((trichlorosilyl)methyl)-3-phenylindane and **4**, were obtained at room temperature. However, the kinetically favored 1,2-cis-2,3-trans isomer was the major product compared to the thermodynamically favorable 1,2-trans-2,3-trans isomer **4** at low reaction temperatures.[18] Since the alkylation reaction of **1g** with **2** requires a reaction temperature of approximately 120 °C, it is reasonable that only the thermodynamically favored trans−trans isomer was obtained. Similarly, the trans−trans isomer with a high degree of stereospecificity was obtained from the cyclization of *β*-methylstyrene and explained by steric hindrance among the substituents.[19]

When **2** reacted with a 6-fold excess of **1g**, 3,3-bis-(2,3,4,5-tetrachlorophenyl)-1,1,1-trichloro-1-silapropane (**3g**) was only detected in trace amounts by GC-MS analysis. Regardless of the molar ratio of the two reactants, the cyclized indane-type products were always obtained as the major products. Attempts to alkylate 1,2,4,5-tetrachlorobenzene with **2** failed, likely due to steric hindrance between two chlorine substituents and the incoming alkyl cation.

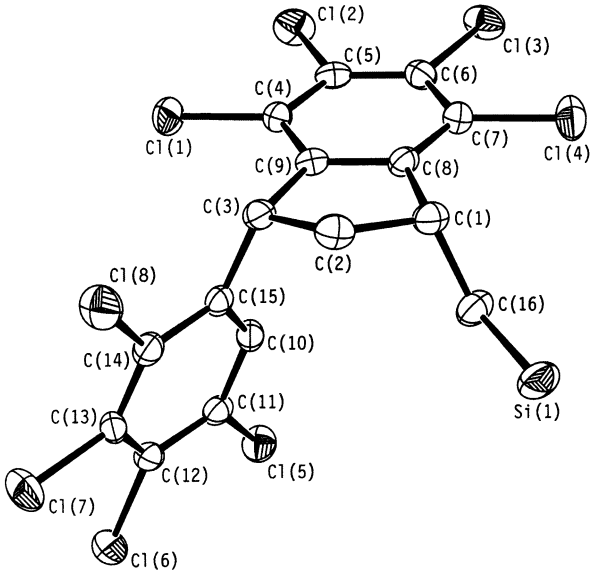


Figure 3. Molecular structure of (1*S*,3*S*)-**7** (ellipsoids represent 30% probability level; hydrogen atoms are omitted for clarity). Only one enantiomer of the racemic mixture is shown.

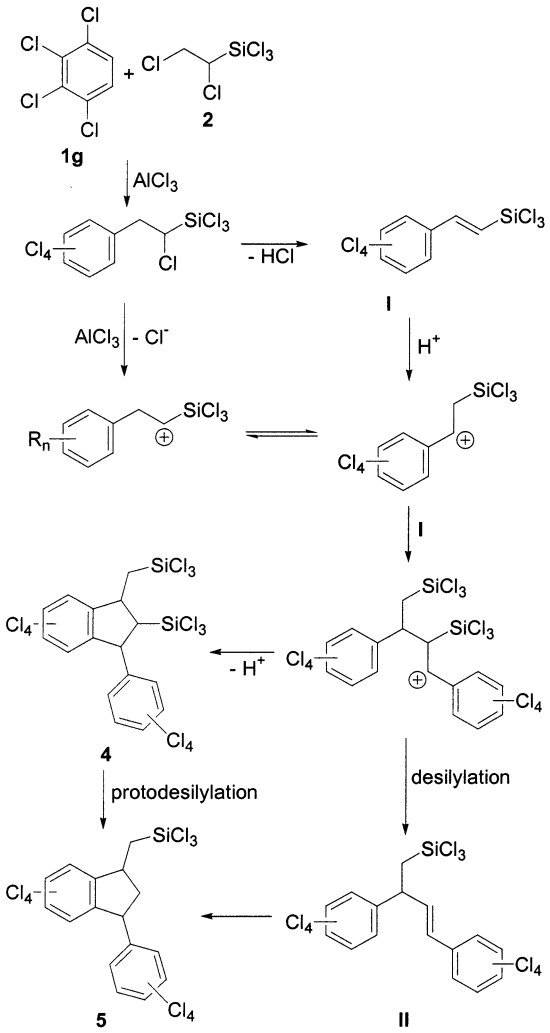
Experimental Section

All reactions and manipulations were carried out under nitrogen using cannula techniques. Solvents were dried according to standard procedures. Aluminum chloride (EP grade) was purchased from Junsei Chemical Co. and used without further purifications. Compound **2** was prepared according to the procedures previously described.[20] All other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. The reaction products were analyzed by GLC using a packed column (10% OV-101 on 80−100 mesh Chromosorb W/AW, $^1/_8$ in. × 1.5 m) or a capillary column (HP-1, 0.11 μm, ID 0.2 mm × 25 m) with a Varian 3300 gas chromatograph equipped with a thermal conductivity detector. NMR spectra were recorded on a Bruker Avance 300 spectrometer (300 MHz for ^{1}H; 75 MHz for ^{13}C) using $CDCl_3$ as a solvent. The chemical shifts are given in ppm relative to the residual proton signal of the solvent: $CDCl_3$ 7.25 ppm (^{1}H) and 77.0 ppm (^{13}C). Melting points (uncorrected) were measured with a Mel-Temp II melting point apparatus using sealed capillary tubes. GC-MS data were obtained with a HP6890/5973 system (70 eV, EI). Elemental analyses were performed by the Advanced Analysis Center of the Korea Institute of Science and Technology. High-resolution mass spectra (EI) were obtained at the Korea Basic Science Institute, Seoul, Korea, on a JEOL JMS-700 mass spectrometer at an ionizing voltage of 70 eV.

General Procedure for the Alkylation of 1 with 2. In a typical experiment, **2** was added to the mixture of aromatic compound **1** (6-fold excess to **2**) and aluminum chloride (10 mol % to **2**) at room temperature under nitrogen. The reaction mixture was heated to 120 °C and stirred for 20 min. Hydrogen chloride gas was evolved during alkylation. After cooling to room temperature, phosphorus oxychloride (the same molar amount for the aluminum chloride used) and hexane were added to the reaction mixture. The reaction mixture was refluxed for 10 min, and the complex was filtered off. Hexane was removed from the filtrate by simple distillation, and the residue was bulb-to-bulb-distilled under vacuum to give the crude product mixture. The crude mixture was vacuum-distilled to give products **3**.

Reaction of 1a with 2. Using the general procedure above, the reaction of **1a** (30.8 g, 274 mmol) and **2** (10.6 g, 45.6 mmol) gave a mixture of six isomers of **3a** (11.9 g, 139−140 °C/0.5 mmHg) as a colorless viscous liquid in 68% yield (based on **2**) in a ratio of 0.6:1.3:13.1:15.1:32.7:37.1 (GC-MSD data). Isolation of the major isomer failed due to the similarity of the boiling points. Data for a mixture of the six isomers of [2,2-bis(chlorophenyl)ethyl]trichlorosilanes (**3a**): ^{1}H NMR ($CDCl_3$) δ 2.21−2.28 (m, 2 H, CH_2Si), 4.31−4.70, 4.92−4.98 (m, 1 H, CHCH$_2$), 7.13−7.38 (m, 8 H, Ar *H*); ^{13}C NMR ($CDCl_3$) δ 30.6, 30.8, 30.9 (*C*H$_2$Si), 40.9, 41.2, 44.9, 45.2 (*C*HCH$_2$), 125.6, 125.7, 127.2, 127.3, 127.7, 128.4, 128.8, 128.9, 129.0, 129.3, 130.1, 130.1, 133.0, 134.5, 134.7, 140.4, 141.5, 141.9, 144.3, 145.1, 145.5 (Ar *C*); MS (70 eV, EI) *m*/*z* (%) [388 (4.4), 386 (13), 384 (19), 382 (12), M$^+$], [235 (100), 237 (68), 239 (12), (M − CH$_2$SiCl$_3$)$^+$]; HRMS (EI) *m*/*z* calcd for $C_{14}H_{11}{}^{35}Cl_5Si$ (M$^+$) 381.9073, found 381.9066. Anal. Calcd for $C_{14}H_{11}Cl_5Si$: C, 43.72; H, 2.88. Found: C, 43.78; H, 2.87.

Scheme 3



Reaction of 1b with 2. Using the general procedure above, the reaction of **1b** (40.3 g, 274 mmol) and **2** (10.6 g, 45.6 mmol) gave a mixture of three isomers of **3b** (12.7 g, 177−179 °C/0.5 mmHg) as a colorless viscous liquid in 61% yield (based on **2**) in a ratio of 0.5:32.4:67.1 (GC-MSD data). Data for the major isomer, [2,2-bis(3,4-dichlorophenyl)ethyl]trichlorosilane: ^{1}H NMR ($CDCl_3$) δ 2.19 (d, J = 7.7 Hz, 2 H, CH_2Si), 4.30 (t, J = 7.7 Hz, 1 H, CHCH$_2$), 7.08 (dd, J = 8.3, 2.1 Hz, 2 H, Ar *H*), 7.33 (d, J = 2.1 Hz, 2 H, Ar *H*), 7.38 (d, J = 8.3 Hz, 2 H, Ar *H*); ^{13}C NMR ($CDCl_3$) δ 30.6 (*C*H$_2$Si), 44.2 (*C*HCH$_2$), 126.8, 129.4, 130.9, 131.5, 133.0, 142.9 (Ar *C*); MS (70 eV, EI) *m*/*z* (%) [458 (2.2), 456 (6.6), 454 (12), 452 (12), 450 (5.4), M$^+$], [309 (12), 307 (51), 305 (100), 303 (80), (M − CH$_2$SiCl$_3$)$^+$]; HRMS (EI) *m*/*z* calcd for $C_{14}H_9{}^{35}Cl_7Si$ (M$^+$) 449.8293, found 449.8311.

Anal. Calcd for $C_{14}H_9Cl_7Si$: C, 37.08; H, 2.00. Found: C, 37.24; H, 2.00.

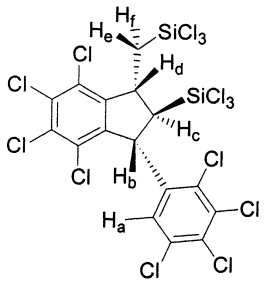
Reaction of 1c with 2. Using the general procedure above, the reaction of **1c** (40.3 g, 274 mmol) and **2** (10.6 g, 45.6 mmol) gave a mixture of three isomers of **3c** (13.0 g, 168−170 °C/0.5 mmHg) as a colorless viscous liquid in 63% yield (based on **2**) in the ratio 1.0:12.4:86.6 (GC-MSD data). Data for the major isomer, [2,2-bis(2,4-dichlorophenyl)ethyl]trichlorosilane: ^{1}H NMR ($CDCl_3$) δ 2.17 (d, J = 7.7 Hz, 2 H, CH_2Si), 5.26 (t, J = 7.7 Hz, 1 H, CHCH$_2$), 7.14 (d, J = 8.4 Hz, 2 H, Ar *H*), 7.23 (dd, J = 8.4, 2.1 Hz, 2 H, Ar *H*), 7.41 (d, J = 2.1 Hz, 2 H, Ar *H*); ^{13}C NMR ($CDCl_3$) δ 29.6 (*C*H$_2$Si), 38.1 (*C*HCH$_2$), 127.2, 129.6, 130.0, 133.7, 134.9, 137.7 (Ar *C*); MS (70 eV, EI) *m*/*z* (%) [456 (5.4), 454 (9.9), 452 (10), 450 (4.5), M$^+$], [309 (13), 307 (52), 305 (100), 303 (79), (M − CH$_2$SiCl$_3$)$^+$]; HRMS (EI) *m*/*z* calcd for $C_{14}H_9{}^{35}Cl_7Si$ (M$^+$) 449.8293, found 449.8282. Anal. Calcd for $C_{14}H_9Cl_7Si$: C, 37.08; H, 2.00. Found: C, 37.36; H, 2.02.

Reaction of 1d with 2. Using the general procedure above, the reaction of **1d** (40.3 g, 274 mmol) and **2** (10.6 g, 45.6 mmol) gave **3d** (14.3 g) as a white solid in 69% yield (based on **2**). Data for **3d**: bp 168−170 °C/0.5 mmHg; mp 112−114 °C; ^{1}H NMR ($CDCl_3$) δ 2.16 (d, J = 7.7 Hz, 2 H, CH_2Si), 5.26 (t, J = 7.7 Hz, 1 H, CHCH$_2$), 7.19 (d, J = 2.4 Hz, 2 H, Ar *H*), 7.21 (dd, J = 8.7, 2.1 Hz, 2 H, Ar *H*), 7.33 (d, J = 8.7 Hz, 2 H, Ar *H*); ^{13}C NMR ($CDCl_3$) δ 29.6 (*C*H$_2$Si), 39.0 (*C*HCH$_2$), 128.8, 129.0, 131.3, 132.5, 133.0, 140.6 (Ar *C*); MS (70 eV, EI) *m*/*z* (%) [458 (2.6), 456 (8.0), 454 (15), 452 (16), 450 (6.8), M$^+$], [309 (12), 307 (50), 305 (100), 303 (77), (M − CH$_2$SiCl$_3$)$^+$]; HRMS (EI) *m*/*z* calcd for $C_{14}H_9{}^{35}Cl_7Si$ (M$^+$) 449.8293, found 449.8295. Anal. Calcd for $C_{14}H_9Cl_7Si$: C, 37.08; H, 2.00. Found: C, 37.19; H, 1.98.

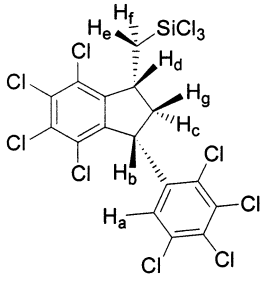
Reaction of 1e with 2. Using the general procedure above, the reaction of **1e** (49.7 g, 274 mmol) and **2** (10.6 g, 45.6 mmol) gave a mixture of two isomers of **3e** (16.4 g, 168−70 °C/0.5 mmHg) as a white solid in 65% yield (based on **2**) in the ratio 8.1:91.9 (GC-MSD data). The major isomer, [2,2-bis(2,3,4-trichlorophenyl)ethyl]trichlorosilane, was isolated by repeated recrystallizations from hexane as colorless crystals: mp 149−151 °C; ^{1}H NMR ($CDCl_3$) δ 2.15 (d, J = 7.7 Hz, 2 H, CH_2Si), 5.31 (t, J = 7.7 Hz, 1 H, CHCH$_2$), 7.04 (d, J = 8.4 Hz, 2 H, Ar *H*), 7.37 (d, J = 8.4 Hz, 2 H, Ar *H*); ^{13}C NMR ($CDCl_3$) δ 29.4 (*C*H$_2$Si), 40.8 (*C*HCH$_2$), 126.8, 128.1, 132.9, 133.4, 134.3, 139.5 (Ar *C*); MS (70 eV, EI) *m*/*z* (%) [526 (4.0), 524 (7.8), 522 (11), 520 (8.1), 518 (2.9), M$^+$], [379 (9.2), 377 (36), 375 (81), 373 (100), 371 (54), (M − CH$_2$SiCl$_3$)$^+$]; HRMS (EI) *m*/*z* calcd for $C_{14}H_7{}^{35}Cl_9Si$ (M$^+$) 517.7514, found 517.7520. Anal. Calcd for $C_{14}H_7Cl_9Si$: C, 32.19; H, 1.35. Found: C, 32.31; H, 1.36.

Reaction of 1f with 2. Using the general procedure above, the reaction of **1f** (49.7 g, 274 mmol) and **2** (10.6 g, 45.6 mmol) gave a mixture of three isomers of **3f** (15.7 g, 168−170 °C/0.5 mmHg) as a colorless viscous liquid in 62% yield (based on **2**) in the ratio of 1:3.7:8.7 (GC-MSD data). The major isomer, [2,2-bis(2,4,5-trichlorophenyl)ethyl]trichlorosilane, was isolated by repeated recrystallizations from hexane as colorless crystals: mp 149−151 °C; ^{1}H NMR ($CDCl_3$) δ 2.12 (d, J = 7.7 Hz, 2 H, CH_2Si), 5.14 (t, J = 7.7 Hz, 1 H, CHCH$_2$), 7.26, 7.52 (s, 4 H, Ar *H*); ^{13}C NMR ($CDCl_3$) δ 29.5 (*C*H$_2$Si), 38.4 (*C*HCH$_2$), 130.1, 131.5, 131.6, 132.5, 132.8, 138.7 (Ar *C*); MS (70 eV, EI) *m*/*z* (%) [526 (3.3), 524 (8.0), 522 (9.5), 520 (7.8), 518 (2.5), M$^+$], [379 (8.2), 377 (35), 375 (79), 373 (100), 371 (52), (M − CH$_2$SiCl$_3$)$^+$]; HRMS (EI) *m*/*z* calcd for $C_{14}H_7{}^{35}Cl_9Si$ (M$^+$) 517.7514, found 517.7510. Anal. Calcd for $C_{14}H_7Cl_9Si$: C, 32.19; H, 1.35. Found: C, 32.39; H, 1.37.

Alkylation of 1g with 2. To a stirred mixture of **1g** (7.21 g, 33.4 mmol) and aluminum chloride (0.44 g, 3.3 mmol) maintained at 70 °C was added **2** (15.4 g, 66.3 mmol), and the reaction mixture was heated to 120 °C. A vigorous reaction started, and hydrogen chloride gas was evolved rapidly. After 10 min, evolution of hydrogen gas ceased, the reaction mixture was cooled to room temperature, and phosphorus oxychloride (0.51 g, 3.3 mmol) and dried *n*-hexane (50 mL) were added and refluxed for 10 min, followed by filtration of the reaction mixture. Solvent and low-boiling portions were removed from the filtrate by simple distillation, and the residue was bulb-to-bulb-distilled under vacuum to give 1.29 g of a low-boiling colorless liquid fraction and 9.40 g of a high-boiling yellow resin-like fraction. Unreacted **1g** (0.81 g, 3.8 mmol) was recovered from the low-boiling fraction. The high-boiling fraction was dissolved in hot hexane (30 mL) and then was kept at −20 °C until the products crystallized. The solid was isolated from the mother liquor, washed with a small amount of hexane, and dried under vacuum to give 8.59 g of colorless solid. The solid was confirmed as a 1.1:1 mixture of **4** and **5** by ^{1}H NMR analysis. Calculated yields were 44% for **4** and 40% for **5** based on **1g** reacted. Compound **4** has a tendency to crystallize first from a mixed solution; therefore, pure **4** and **5** were isolated as colorless crystals by repeated recrystallizations from hexane, respectively. Data for *rac*-1,2-*trans*-2,3-*trans*-4,5,6,7-tetrachloro-1-(2,3,4,5-tetrachlorophenyl)-2-(trichlorosilyl)-3-((trichlorosilyl)methyl)indane (**4**):



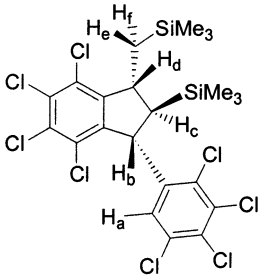
mp 210−212 °C; ^{1}H NMR ($CDCl_3$) δ 1.39 (dd, J = 15.3, 11.5 Hz, 1 H, H$_f$), 2.10 (dd, J = 15.3, 1.8 Hz, 1 H, H$_e$), 2.59 (s, 1 H, H$_c$), 4.08 (br d, J = 11.5 Hz, H$_d$), 5.10 (s, 1 H, H$_b$), 6.56 (s, 1 H, H$_a$); ^{13}C NMR ($CDCl_3$) δ 29.6 (*C*H$_2$Si), 42.0, 43.9, 50.2 (cyclic *C*), 126.7, 128.9, 129.9, 132.1, 132.7, 132.9, 133.5, 134.2, 134.9, 139.4, 139.7, 145.2 (Ar *C*); MS (70 eV, EI) *m*/*z* (%) [754 (3.2), 752 (4.3), 750 (5.4), 748 (3.9), 746 (1.9), M$^+$], [609 (6.2), 607 (19), 605 (40), 603 (60), 601 (61), 599 (40), 597 (11), (M − CH$_2$SiCl$_3$)$^+$], [139 (4.1), 137 (32), 135 (94), 133 (100), SiCl$_3^+$]; HRMS (EI) *m*/*z* calcd for $C_{16}H_6{}^{35}Cl_{14}Si_2$ (M$^+$) 743.5647, found 743.5640. Anal. Calcd for $C_{16}H_6Cl_{14}Si_2$: C, 25.60; H, 0.81. Found: C, 25.77; H, 0.85. Data for *rac*-1,3-*cis*-4,5,6,7-tetrachloro-1-(2,3,4,5-tetrachlorophenyl)-3-((trichlorosilyl)methyl)indane (**5**):



mp 175−178 °C; ^{1}H NMR ($CDCl_3$) δ 1.26 (dd, J = 15.4, 11.9 Hz, 1 H, H$_f$), 2.12 (dd, J = 15.4, 1.3 Hz, 1 H, H$_e$), 2.17 (br d, J = 14.2 Hz, 1 H, H$_c$), 3.03 (ddd, J = 14.2, 9.8, 9.8 Hz, 1 H, H$_g$), 3.75 (dddd, J = 11.9, 9.8, 1.5, 1.3 Hz, 1 H, H$_d$), 4.88 (dd, J = 9.8, 1.5 Hz, 1 H, H$_b$) 6.61 (s, 1 H, H$_a$); ^{13}C NMR ($CDCl_3$) δ 29.5 (*C*H$_2$Si), 38.2, 40.4, 49.2 (cyclic *C*), 125.9, 129.1, 130.0, 131.8, 132.0, 132.5, 132.7, 133.4, 134.4, 140.5, 141.5, 146.7 (Ar *C*); MS (70 eV, EI) *m*/*z* (%) [622 (4.0), 620 (8.0), 618 (13), 616 (14), 614 (8.1), 612 (2.4), M$^+$], [475 (7.0), 473 (27), 471 (64), 469 (100), 465 (36), (M − CH$_2$SiCl$_3$)$^+$]; HRMS (EI) *m*/*z* calcd for $C_{16}H_7{}^{35}Cl_{11}Si$ (M$^+$) 611.6891, found 611.6898. Anal. Calcd for $C_{16}H_7Cl_{11}Si$: C, 31.13; H, 1.14. Found: C, 31.35; H, 1.13.

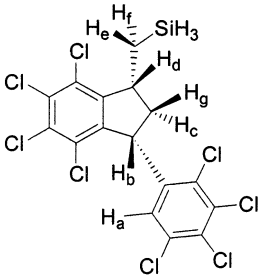
Methylation of 4 with Methylmagnesium Chloride. To a solution of **4** (2.38 g, 3.17 mmol) in THF (30 mL) at 0 °C was added dropwise a 3 M solution of methylmagnesium chloride

in THF (7.4 mL, 22 mmol) for 10 min. The reaction mixture was stirred at room temperature for 30 min, treated with 5% ammonium chloride solution, and extracted with hexane. The extracts were washed with brine and dried over anhydrous $MgSO_4$. Solvents were removed. The residue was dissolved in hexane. Recrystallizations from hexane solution afforded **6** (1.31 g) as colorless crystals in 66% yield. Data for *rac*-1,2-*trans*-2,3-*trans*-4,5,6,7-tetrachloro-1-(2,3,4,5-tetrachlorophenyl)-2-(trimethylsilyl)-3-((trimethylsilyl)methyl)indane (**6**):



mp 183−184 °C; ^{1}H NMR ($CDCl_3$) δ −0.06 (s, 9 H, SiCH_3), −0.03 (s, 9 H, SiCH_3), 0.51 (dd, J = 13.9, 11.8 Hz, 1 H, H_f), 1.10 (br d, J = 13.9 Hz, 1 H, H_e), 1.56 (s, 1 H, H_c), 3.40 (br d, J = 11.8 Hz, H_d), 4.66 (s, 1 H, H_b), 6.62 (s, 1 H, H_a); ^{13}C NMR ($CDCl_3$) δ −2.1, −1.0 (SiCH_3), 24.2 (CH_2Si), 38.8, 44.5, 51.5 (cyclic *C*), 127.5, 128.4, 129.3, 131.2, 131.4, 131.9, 132.8, 133.8, 140.7, 143.1, 150.7 (Ar *C*); MS (70 eV, EI) *m*/*z* (%) [630 (1.6), 628 (1.9), 626 (1.5), M^+], [619 (2.3), 617 (6.5), 615 (14), 613 (19), 611 (19), 609 (7.5), $(M - CH_3)^+$], [547 (8.1), 545 (26), 543 (66), 541 (100), 539 (91), 537 (41), $(M - CH_2SiMe_3)^+$]; HRMS (EI) *m*/*z* calcd for $C_{21}H_{21}{}^{35}Cl_8Si_2$ ($M - CH_3^+$) 608.8690, found 608.8714. Anal. Calcd for $C_{22}H_{24}Cl_8Si_2$: C, 42.06; H, 3.85. Found: C, 42.12; H, 3.86.

Reduction of 5 with Lithium Aluminum Hydride. To a suspension of lithium aluminum hydride (0.19 g, 5.0 mmol) in THF (30 mL) at 0 °C was added a solution of **5** (1.82 g, 2.95 mmol) in THF (15 mL) dropwise for 15 min. The reaction mixture was stirred at room temperature for 40 min, hydrolyzed with 5% ammonium chloride solution, and extracted with hexane. The extract was washed with brine and dried over anhydrous $MgSO_4$. Solvents were evaporated, and the residue was dissolved in THF. Recrystallizations from THF solution afforded **7** (1.12 g) as colorless crystals in 74% yield. Data for *rac*-1,3-*cis*-4,5,6,7-tetrachloro-1-(silylmethyl)-3-(2,3,4,5-tetrachlorophenyl)indane (**7**):



mp 220−226 °C; ^{1}H NMR ($CDCl_3$) δ 0.56−0.69 (br m, 1 H, H_f), 1.47−1.53 (br m, 1 H, H_e), 1.89 (br d, J = 13.9 Hz, 1 H, H_c), 2.97 (ddd, J = 13.9, 10.0, 10.0 Hz, 1 H, H_g), 3.44 (br d, J = 10.0 Hz, 1 H, H_d), 3.48 (t, J = 3.6 Hz, 3 H, SiH_3) 4.84 (dd, J = 10.0, 1.7 Hz, 1 H, H_b) 6.66 (s, 1 H, H_a); ^{13}C NMR ($CDCl_3$) δ 12.8 (CH_2Si), 38.5, 43.6, 49.1 (cyclic *C*), 126.3, 129.2, 129.8, 131.4, 131.87, 131.92, 132.3, 133.1, 134.0, 140.2, 142.2, 148.7 (Ar *C*); MS (70 eV, EI) *m*/*z* (%) [518 (7.3), 516 (19), 514(28), 512 (26), 510 (10), M^+], [477 (5.6), 475 (8.8), 473 (25), 471 (65), 469 (100), 467 (91), 465 (35), $(M - CH_2SiH_3)^+$]; HRMS (EI) *m*/*z* calcd for $C_{16}H_{10}{}^{35}Cl_8Si$ (M^+) 509.8060, found 509.8067. Anal. Calcd for $C_{16}H_{10}Cl_8Si$: C, 37.39; H, 1.96. Found: C, 37.58; H, 2.01;

Table 2. Crystallographic Details for 4, 6, and 7

	4	**6**	**7**
formula	$C_{16}H_6Cl_{14}Si_2$	$C_{22}H_{24}C_{18}Si_2$	$C_{16}H_{10}C_{18}Si$
fw	750.69	628.19	513.93
cryst size, mm	0.37 × 0.35 × 0.21	0.58 × 0.42 × 0.15	0.45 × 0.20 × 0.71
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	8.751(2)	8.9103(2)	8.3997(2)
b, Å	12.110(3)	12.4270	11.3458(3)
c, Å	13.516(4)	13.7735(1)	11.4398(3)
α, deg	81.684(5)	81.6290(10)	68.4530(10)
β, deg	84.035(5)	84.5000(10)	83.3100(10)
γ, deg	76.512(5)	76.3630(10)	85.678(2)
Z	2	2	2
d_{calcd}, g cm^{-3}	1.814	1.426	1.693
μ(Mo Kα), mm^{-1}	1.499	0.863	1.175
θ, deg	1.5−28.3	1.5−23.2	1.9−24.6
no. of indep rflns	5650	4099	3349
no. of obsd data ($I > 2\sigma(I)$)	3646	3103	2626
no. of params	293	295	227
R1(F)[a]	0.0492	0.0516	0.0631
wR2(F)[a]	0.1217	0.1391	0.1805
GOF	0.96	1.05	1.04
largest diff peak, hole, e Å^{-3}	−0.38, 0.46	−0.38, 0.31	−0.63, 0.43

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. For **4**, $w = 1/[\sigma^2(F_o^2) + (0.064P)^2]$, where $P = [F_o^2 + 2F_c^2]/3$. For **6**, $w = 1/[\sigma^2(F_o^2) + (0.0714P)^2]$, where $P = [F_o^2 + 2F_c^2]/3$. For **7**, $w = 1/[\sigma^2(F_o^2) + (0.1096P)^2 + 0.3111P]$, where $P = [F_o^2 + 2F_c^2]/3$.

X-ray Crystallographic Studies. The single crystals of compounds **4**, **6**, and **7** for X-ray crystallographic analyses were obtained from their hexane or THF solutions, as described above. The X-ray crystallographic analyses were carried out with a Siemens SMART diffractometer/CCD area detector employing a 3 kW sealed-tube X-ray source operating at 1.5 kW and centered in the beam. The structures were solved and refined with the SHELX-97 program using direct methods and expanded using Fourier techniques.[21] All non-hydrogen atoms were refined with anisotropic thermal parameters in the later stages of refinement. All hydrogen atoms except those of methyl groups were placed in idealized positions and refined using the riding model with general isotopic temperature factors. Details of the crystal data and a summary of intensity data collection parameters are given in Table 2.

Acknowledgment. This research was supported financially by Dow Corning Corp. We thank Prof. D. Son of Southern Methodist University, Dallas, TX, for his help and discussions in the preparation of this paper.

Supporting Information Available: Tables giving full details of the crystallographic data and data collection parameters, atom coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen coordinates for **4**, **6**, and **7** and figures giving low-resolution MS spectra of **3a**−**f** and **4**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020296C