Friedel–Crafts Alkylation of Substituted Benzenes by Allyldichlorosilane

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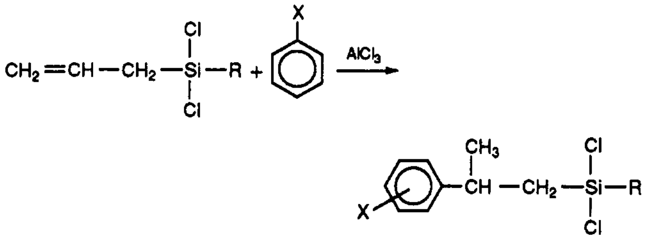
A Friedel–Crafts type reaction of substituted benzenes with allyldichlorosilane in the presence of aluminum chloride as a catalyst resulted in alkylation, giving 3-aryl-1,1-dichloro-1-silabutanes in good yields (60–85%). All the isomeric products derived from the alkylation were identified and the relative alkylation rates of substituted benzenes were determined by GLC. The alkylation of substituted benzenes with allyldichlorosilane at temperatures below 0 °C gave *ortho-* and *para*-directing products at an early stage, but the products isomerized to the *meta* isomer as the reaction proceeded for prolonged times or at moderately higher reaction temperature. The competitive alkylation rates of substituted benzenes having various substituents (X) decreased in the following order: X = Ph > PhO > *i*-Pr > Et > Me > H > F > Cl > Br. When the alkylation rates of substituted benzenes with respect to benzene (log k_x/k_H) were plotted against the substituent coefficients (σ), a good linear relationship was observed. The results showed that electron-donating groups on the benzene ring generally facilitate the alkylation, while electron-withdrawing groups are deactivating. This alkylation method is a good route to (2-arylpropyl)-dichlorosilanes having a Si–H functionality groups into the silanes.

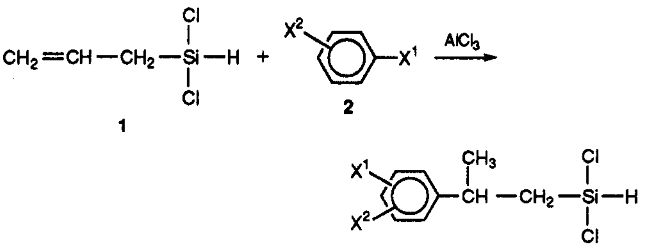
Introduction

Alkylations of aromatic compounds with an olefin in the presence of a Lewis acid catalyst have been reported in many articles[2] since the alkylation of benzene with ethylene was reported for the first time by Balsohn in 1879.[3] Some of the reactions have been utilized on a large scale for industrial production.[4–10] However, the alkylation of aromatic compounds with alkenylsilanes has attracted little attention because of the low reactivity of vinylsilanes[11,12] and the difficulties of allylsilane syntheses.[13,14] The reaction conditions for alkylation of benzene systems with vinylsilanes[15] required relatively high reaction temperatures (above 75 °C) and prolonged reaction time.[11,12] The alkylation of benzene systems with allylsilanes was first reported by the Nametkin group.[16] (2-Arylpropyl)-silanes were obtained on reaction of allylchlorosilanes, such as allyldichlorosilane (1) and allyltrichlorosilane, with substituted benzenes. The yields ranged from 34% to 66%, depending upon the benzene ring substituents, but information concerning reaction rates and product isomer distribution was not reported.



R = H, Cl

Recently, we reported the direct synthesis of 1 by the reaction of a mixture of allyl chloride and hydrogen chloride with elemental silicon in the presence of copper catalyst.[17]



3–15

X^1 = H, Me; X^2 = H, Me, Et, *i*-Pr, F, Cl, Br, OPh, Ph

The success of this direct synthesis has made 1 readily

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available, and this prompted us to investigate the Friedel–Crafts type alkylation of aromatic compounds with 1. Allyldichlorosilane has four functional groups of three different kinds, and (2-arylpropyl)dichlorosilanes containing a Si–H bond would be of interest. These compounds could find useful applications as starting materials for new silicones. In this investigation we have studied the alkylation of substituted benzenes with 1 and report substituent effects of benzene ring systems, reaction rates, and isomer distributions of the products.

Results and Discussion

Nature of the Allylsilane. The reactivities of allylsilanes in Friedel–Crafts type alkylations of aromatic compounds varied, depending on the substituents on silicon.[16] Allylchlorosilanes having two or more chlorine atoms on silicon such as 1, allylmethyldichlorosilane, and allyltrichlorosilane readily reacted with substituted benzenes to give (2-arylpropyl)silanes in the presence of aluminum chloride, but allyltrimethylsilane did not do so.[16] Chloro- or bromobenzene also reacted with allyltrichlorosilane and allyldichlorosilane but required higher reaction temperatures and gave lower yields than alkylbenzenes. We examined the reactions of benzene with allyldimethylchlorosilane and allyldimethylsilane, but no alkylation products were detected,[18] suggesting that the alkylation of benzene by allylchlorosilanes requires at least two chlorine substituents on the silicon atom.

In Friedel–Crafts alkylation with alkenes in the presence of aluminum chloride as a catalyst, a small amount of hydrogen chloride resulting from the reaction of anhydrous aluminum chloride with water inevitably present in the reaction mixture initiates the reaction.[19] The proton resulting from hydrogen chloride and aluminum chloride will interact with the π bond of allylsilanes to give the carbonium ion on the carbon β to silicon, because the silylethyl cation is stabilized by the electron-donating silyl group through the σ–π conjugation.[20] This electrophilic attack on the π bond of allylsilanes to generate cationic intermediates is well accepted.[21] The β-stabilization will be more effective for allyltrimethylsilane than allylchlorosilanes because of the electron-donating methyl groups on silicon. This facilitates the protodesilylation of allyltrimethylsilane[22] rather than the alkylation reactions with benzene. In contrast, in allyltrichlorosilane, the collapse of the β-silyl cation intermediate is largely retarded due to the less effective σ–π conjugation by the presence of the electronegative chlorine atoms on silicon. This seems to cause the β-silyl cation to react with benzene faster than the protodesilylation reaction.

Alkylation of Substituted Benzenes with Allyldichlorosilane (1). The alkylation of substituted benzenes with 1 in the presence of aluminum chloride catalyst at 0 °C or at room temperature gave monoadducts, 3-aryl-1,1-dichloro-1-silabutanes, along with a small amount of diadducts. The isolated yields were very good, ranging from 60% to 85% depending upon the substituents on the benzene ring. The diadduct products obtained usually amounted from 2% to 8%, when a 5-fold excess[23] of the aromatic compound with respect to 1 was used. The amount of diadduct could be reduced further by using a greater excess of the aromatic compound. The results of these alkylation reactions are summarized in Table 1.

Table 1. Alkylation Conditions and Isomer Distributions of Products[a]

entry no.	substituent X^1	substituent X^2	reacn temp (°C)	reacn time (min)	yields (%)	isomer distribn *o:m:p*	product code[b]
1	H	H	room temp	20	72		**3**
2	H	Me	0	20	70	3:66:31	**4a–c**
3	H	Et	0	20	78	2:64:34	**5a–c**
4	H	*i*-Pr	0	20	71	–:33:67	**6b,c**
5	H	*p*-Ph[c]	room temp	20	83	–:37:63	**7b,c**
6	H	*p*-PhO[c]	room temp	20	74	47:3:50	**8a–c**
7	H	F	room temp	50	69	31:2:67	**9a–c**
8	H	Cl	room temp	50	68	27:6:67	**10a–c**
9	H	Br	room temp	50	60	29:9:62	**11a–c**
10	Me	*p*-Me	0	20	81		**12**
11	Me	*m*-Me	0	20	73	**ac**:**bb** = 62:38	**13ac,bb**
12	Me	*o*-Me	0	20	85	**ab**:**bc** = 2:98	**14ab,bc**
13	Me	*p*-Cl	0	20	66	**ab**:**ba** = 80:20	**15ab,ba**

[a] Mole ratio **1**:aromatic compound:aluminum chloride = 1:5:0.1. [b] **a–c** represent *ortho-*, *meta-*, and *para*-substituted products, respectively. [c] The reaction was carried out in hexane solution.

As shown in Table 1, the alkylation of alkylbenzenes with 1 was complete within 20 min at 0 °C to give the monoadducts in 70–78% yield, but the reaction with halobenzenes required longer times at higher temperatures. The yields from halobenzene reactions at room temperature for 50 min ranged from 60% to 66%. The Friedel–Crafts reactions of biphenyl and diphenyl ether were carried out in *n*-hexane solution at room temperature. The results indicate that electron-donating alkyl groups on benzene ring generally facilitate the alkylation, while electron-withdrawing substituents such as halogens are deactivating.[5,24] This is consistent with an electrophilic substitution process.

Identifications of Isomers. Products obtained in the alkylation of substituted benzenes with 1 were distilled under vacuum. GLC analysis of distillates indicated the monoadducts of 1 with the benzene ring were obtained predominantly as a mixture of isomeric products. GC/MS spectra of the isomeric products obtained from each reaction showed the same fragmentation patterns with the same relative peak intensities. This suggests each reaction product is a mixture of the expected *ortho*, *meta*, and *para* isomers.[10,25] The product isomer ratio was determined with GLC, and the isomers were purified by preparative GLC. Subsequent NMR spectral analysis allowed assignment of the structure of each isomer. Those isomers obtained in less than 3% yield could not be separated by preparative GLC, but their structures were assigned by comparing the GC/MS spectra with those of the already identified isomers.

In the identification of isomers, the ^{1}H NMR chemical shift of the methine hydrogen on the carbon atom β to silicon was very helpful. In ^{1}H NMR spectra of alkylated products the methine proton signal was a hextet due to splitting by the five protons on the adjacent two carbon

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(18) A Friedel–Crafts reaction of allylchlorodimethylsilane with benzene gave polymeric material.

(19) Thomas, C. A. *Anhydrous Aluminum Chloride in Organic Chemistry*; Reinhold: New York, 1941.

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(21) Eabon, C.; Bott, R. W. In *Organometallic Compounds of the Group IV Elements*; MacDiarmid, A. G., Ed.; Dekker: New York, 1968; Vol. 1, Part 1, pp 359–437.

(22) Jenkins, P. R.; Gut, R.; Wetter, H.; Eschenmoser, A. *Helv. Chim. Acta* **1979**, *62*, 1922.

(23) As an economical route for the synthesis of (2-arylpropyl)dichlorosilane, the mole ratio of allyldichlorosilane to substituted benzene to aluminum chloride was 1:5:0.1 in alkylation reactions.

(24) (a) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165. (b) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979.

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atoms. The methine hydrogen of *ortho*-substituted isopropylbenzenes appeared notably downfield by about 0.4–1 ppm compared with the signals for the *meta* and *para* isomers.[26] This downfield shift is explained in terms of the higher ring current effect for the methine proton in the case of the *ortho* isomer, where the proton would be positioned toward the *ortho* substituent, nearly coplanar with the ring plane because of the steric interactions between the two substituents. In some cases, the isomer structures were deduced from the identification of the reduced products in which Si–H had been substituted for Si–Cl by reduction with $LiAlH_4$. The reduced compounds are more stable toward the atmosphere and allowed better separation of the isomers by GLC.

In the alkylation of toluene, the products were reduced and the ^1H NMR spectra of the isomeric mixtures were taken. The methine proton signals appeared at 3.17, 2.86, and 2.87 ppm due to the presence of three isomers. The most downfield signal at 3.17 ppm was assigned to the *ortho* isomer in analogy to the downfield shift in *o*-isopropylmethylbenzene compared with the other isomers.[26] In order to confirm this assignment, 1 was reacted with *p*-xylene. Only one product was obtained because the four protons on unsubstituted ring carbons are equivalent. The propyl group of the product should be positioned in a position *ortho* to one of the methyl groups as in the *ortho* product obtained in the alkylation of toluene. The product obtained in the alkylation of *p*-xylene was reduced by lithium aluminum hydride. The methine proton signal of the resulting product appeared at 3.14 ppm, which was similar to the chemical shift assigned to the *ortho* product from toluene, thus confirming the assignment. The characterization of the *meta* and *para* isomers, after their separation by GLC, was effected by comparing their ring proton NMR spectra.[26]

The ratio of *ortho* to the *meta* and *para* products derived from alkylation of monosubstituted alkylbenzenes with 1 decreased as the size of the substituents on the benzene ring increased. No *ortho*-alkylation product was found in the case of isopropylbenzene due to the steric interaction between the isopropyl group and the incoming allyl groups. Steric hindrance arising from the size of the alkyl groups at the *ortho* positions appeared to be the principal cause of the differences in alkylation rates of the substituted benzenes.[25,27] The yield of the *ortho* isomer decreased and that of the *meta* isomer increased among the three isomers as the reaction proceeded for longer times or at higher temperatures in the presence of aluminum chloride, which was consistent with results reported in the literature.[11] The identification procedure for isomers produced in the alkylation of toluene with 1 was applied to other alkylation reactions.

The alkylation of halogen-substituted (X = F, Cl, Br) benzenes with 1 gave *ortho* and *para* adducts predominantly (91–98%). Considering the high electronegativities of halogen atoms, the *meta* isomer was expected to be the major product. The isomerization of the products obtained from alkylbenzenes was faster than that of the products obtained from halobenzenes.

Temperature Dependence of Isomer Distributions. Different isomer distributions of the products derived from the alkylation of toluene were obtained at different reaction temperatures, which could be due to the temperature dependence of isomer formation and/or isomerization reactions of the products. To investigate the redistribution of isomers, the alkylation of 1 with 20-fold excess toluene in the presence of aluminum chloride was carried out at various reaction temperatures from −45 to +20 °C. After alkylation was completed at a certain temperature, the products were reduced using an excess of 1 M lithium aluminum hydride in tetrahydrofuran for both deactivation of catalyst and easy analysis of isomers. The isomers of the alkylation products were characterized by ^1H NMR and ^{13}C NMR data, and the isomer proportion was determined by GLC. The isomer distributions at various reaction temperatures are summarized in Table 2.

Table 2. Temperature and Time Dependence of Isomer Distributions[a]

reacn conditions		isomer distribn (%)		
temp (°C)	time (min)	**4a**	**4b**	**4c**
−45	60	53	9	38
−35	20	47	15	35
0	20	17	20	63
20	20	5	38	57
20	480	3	65	32
20	1200	2	67	31

[a] Mole ratio 1:toluene:aluminum chloride = 1:20:0.1.

As shown in Table 2, the isomer distributions were very different reaction temperatures, as reported for other systems.[10] At low temperatures from −45 to −35 °C, the products were mostly the *ortho* (53% and 47%) and *para* isomers (38% and 35%), which is consistent with the *ortho*- and *para*-directing nature of the methyl group.[28] When the reactions were carried out at temperatures from 0 to 20 °C, the percentage of *ortho* isomer decreased drastically but that of the *meta* and *para* isomers increased. At room temperature, the *meta* isomer content reached 38% and that of the *para* increased to 57%. The percentage of *meta* isomer further increased to 67% as the reaction mixture was left to stand for 20 h, while the *para* isomer decreased again to 31%. The equilibrium of the redistribution seemed to be reached after 20 h at room temperature. These results indicate that the *ortho* product isomerized probably in order to minimize the steric interactions between the bulky 1-methyl-3,3-dichloro-3-silapropyl and the methyl groups, to give thermodynamically the most stable product. Aluminum chloride in Friedel–Crafts reactions has been reported to be an effective catalyst for intra- and intermolecular isomerizations[29] of alkylbenzenes. When the *ortho* isomer of 3-(methylphenyl)-1,1-dichloro-1-silabutane was warmed under the Friedel–Crafts reaction conditions, the *meta* isomer was produced. These results indicate that the alkylation of alkylbenzenes with 1 gave the kinetically controlled products, the *ortho* and *para* adducts, in the early stages and that then the isomerization or alkylation–dealkylation of the resulting alkylated benzenes favored the thermodynamically most stable product, the *meta* adduct, as had been observed in the reaction of toluene with *n*-butene.[10]

Kinetic Study for the Alkylation of Substituted Benzenes. Competitive alkylation reactions of substituted benzenes with 1 were carried out using a 1:1 mixture

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(26) Refer to the spectra of isopropyltoluene: Pouchet, C. J.; Behnke, J. *The Aldrich Library of* ^{13}C *and* ^1H*-FTNMR Spectra*; Aldrich: Milwaukee, WI, 1993; Addition 1, Vol. 2, pp 10–15.

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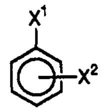
(28) Cullinane, N. M.; Leyshon, D. M. *J. Chem. Soc.* **1954**, 2942.

(29) In fact, treatment of a mixture containing *ortho*, *meta*, and *para* products in excess benzene with aluminum chloride led to the production of 3-phenyl-1,1-dichloro-1-silabutane; see: Tsuge, O.; Tashiro, M. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 119.

Table 3. Relative Alkylation Rates[a] and Substituent Constants[5] (σ) for Substituted Benzenes



substituents		rel rates		substituent const[5]		
X[1]	X[2]	k_x/k_H	$\log(k_x/k_H)$	σ_R	σ_I	σ
H	Br	0.011	−1.96	0.72	−2.52	0.54
H	Cl	0.016	−1.44	0.72	−0.24	0.48
H	F	0.081	−1.04	0.74	−0.60	0.14
H	H	1.00	0.00	0.00	0.00	0.00
H	Me	3.89	0.59	−0.01	−0.41	−0.42
H	Et	4.10	0.61	−0.02	−0.44	−0.46
H	*i*-Pr	5.65	0.72			
H	PhO	9.42	0.97	0.76	−1.29	−0.53
H	Ph	10.27	1.01	0.25	−0.37	−0.12
Me	*o*-Me		0.13			
Me	*m*-Me		0.46			
Me	*p*-Me		0.05			
Me	*p*-Cl		−1.22			

[a] Mole ratio **1**:aromatic compounds:aluminum chloride = 1:20:0.1. Definitions: σ_R, resonance constant; σ_I field constant; $\sigma = \sigma_R + \sigma_I$.

of a substituted benzene and benzene. The mixture was used in 20-fold excess relative to **1** in order to minimize diadduct products. The amount of aluminum chloride catalyst used was 10% of **1**, and the same reaction conditions were used in all experiments. The results are summarized in Table 3.

As Table 3 shows, the rate of alkylation of substituted benzenes (PhX) with **1** decreased in the following order: X = Ph > PhO > *i*-Pr > Et > Me > H > F > Cl > Br.[5] Faster reaction rates for the alkylbenzenes than for the halogen-substituted benzenes were observed, as expected from the electron-donating effect of alkyl substituents. Among the halogen-substituted benzenes, the fastest rate was observed for fluorobenzene and the slowest for bromobenzene, which is not consistent with the electronegativities of the substituents.[5,24] The results indicate that the resonance effects of halogen substituents on the benzene ring should be considered in addition to electronegativity effects in order to explain the reaction rates. However, the order of the rates was in good agreement with those of literature data[5] for alkylation reactions, except for X = Ph.[30] In the case of disubstituted benzenes, the reactivity for alkylation decreased as follows: *m*-xylene > *o*-xylene > *p*-xylene > *p*-chlorotoluene. This result shows also that the rate of alkylation depends on both the steric hindrance and activation abilities of two substituents on the benzene ring, as observed in reactions with monosubstituted benzenes.[2]

The relative reaction rates for the alkylation of substituted benzenes with respect to benzene ($\log k_x/k_H$) are plotted against substituent coefficients (σ)[5] for alkyl, aryl, and halogen groups in Figure 1. As may be seen, a good linear relationship exists for the substituent groups according to the Hammett equation:[31] $\log k_X/k_H = \rho\sigma$, where ρ is the Hammett constant and was calculated to be −3.1. However, the relative reaction rates were not linearly related to inductive coefficients or resonance coefficients alone. The substituent coefficient (σ) of the isopropyl group, which was not reported, could be calculated as −0.47 from the linear relationship in Figure 1 by substituting the alkylation rate of isopropylbenzene. The results show that the rates of alkylation of substituted benzenes with **1** increase with increasing electron donation of the substituent to the benzene ring.[5,24]

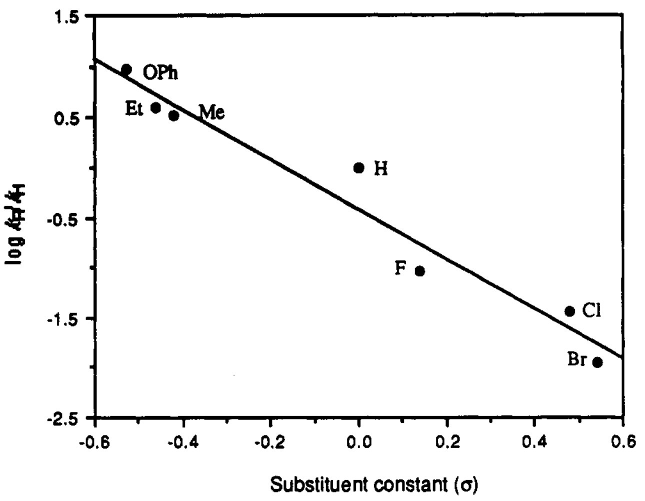


Figure 1. Correlation of relative reaction rate ($\log(k_R/k_H)$) with substituent constant (σ).

Experimental Section

The solvents *n*-hexane and tetrahydrofuran were dried by distillation from sodium benzophenone ketyl. A THF solution of 1 M lithium aluminum hydride was obtained from Aldrich Chemical Co. All reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen. All air-sensitive liquids and dried solvents were transferred by standard syringe or double-tipped-needle techniques. Products obtained from the reaction of allyldichlorosilane with substituted benzenes were analyzed by GLC using a 15- or 30-m capillary column coated with SE-30 or DB-1701 on a Varian 3300 gas chromatograph with a flame ionization detector and a Varian 4290 integrator. The ratio of product isomers was determined by GLC and GC/MS. The samples for characterization were purified by preparative GLC using a Varian Aerograph Series 1400 gas chromatograph with a thermal conductivity detector and a 3 m by $^1/_8$ in. stainless steel column packed with 15% SE-30 or SE-54 on 60–80 mesh Chromosorb W. Proton and carbon NMR spectra were obtained on a Bruker AM 200-SY or a Varian Gem 300 spectrometer in chloroform-*d*. Chemical shifts are reported in parts per million downfield from the internal standard tetramethylsilane. Mass spectra were obtained using a Hewlett-Packard 5980 GC/MS. Elemental analyses were performed by the Chemical Analysis Laboratory of the Korea Institute of Science and Technology. The isomers **4a**, **5a**, and **9b**, produced in less than 3% yield, could not be separated under our preparative GC conditions, but they were characterized by GS/MS because of the difficulty of identification from the analysis of NMR data obtained from the mixture of isomers.

General Procedure for Competition Alkylation. To an equimolar aromatic mixture of benzene (15.6 g, 200 mmol), the substituted benzene (200 mmol), and aluminum chloride (0.13 g, 1 mmol) was added 1.4 g (10 mmol) of **1** dropwise over a period of 3 min at room temperature with thorough stirring. The reaction was allowed to proceed for another 20 min. The reaction mixture was then analyzed by GLC. In the case of biphenyl and diphenyl ether, the competition reaction was carried out in hexane solution.

Synthesis of 3-Phenyl-1,1-dichloro-1-silabutane (3). To 13.9 g (178 mmol) of benzene and 0.4 g (3 mmol) of anhydrous aluminum chloride at room temperature was added slowly, dropwise, 5.0 g (36 mmol) of **1**. The reaction mixture was stirred for 30 min, and 2.0 g (34 mmol) of sodium chloride was added to this mixture, which then was warmed to 70 °C and stirred for 1 h. After the salts were filterd off and the mixture evaporated to remove benzene, vacuum distillation gave **3** (5.7 g, 26 mmol;

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(30) The substituent constant of biphenyl calculated from the relationship of Figure 1 was greater than the literature value.[5]

(31) (a) Hammet, L. P. *Physical Organic Chemistry*; McGraw-Hill: New York, 1940; p 267. (b) Hammett, L. P.; Deyrup, A. J. *J. Am. Chem. Soc.* **1932**, *54*, 2721.

Table 4. Product Properties

compd no.	bp[a] (°C)	anal. calcd (found)	^{1}H NMR (δ)
4a–c	73–76	C, 51.50 (51.19); H, 6.05 (5.94)	1.39, 1.41, and 1.40 (d, J = 7 Hz, 3H, CH_3), 1.60–1.65 (m, 2H, CH_2), 2.32, 2.37, and 2.36 (s, 3H, CH_3), 3.51, 3.15, and 3.15 (hex, J = 7 Hz, 1H, CH), 5.32, 5.34, and 5.33 (t, J = 2 Hz, 1H, Si–H), 7.05–7.27 (m, 4H, phenyl H)
5a–c	82–84	C, 53.44 (53.55); H, 6.42 (6.50)	1.26 (1.25) (t, J = 8 Hz, 3 H, CH_3), 1.41 (1.40) (d, J = 7 Hz, 3H, CH_3), 1.61–1.64 (m, 2H, CH_2), 2.66 (2.64) (q, J = 8 Hz, 2H, CH_2), 3.16 (3.16) (hex, J = 7 Hz, 1H, CH), 5.33 (5.33) (t, J = 2 Hz, 1H, Si–H), 7.05–7.28 (m, 4H, phenyl H)
6b,c	94–96	C, 55.17 (55.11); H, 6.94 (6.77)	1.29 (1.28) (d, J = 7 Hz, 3H, CH_3), 1.42 (1.40) (d, J = 7 Hz, 3H, CH_3), 1.61–1.65 (m, 2H, CH_2), 2.92 (2.90) (hept, J = 7 Hz, 1H, CH), 3.17 (3.16) (hex, J = 7 Hz, 1H, CH), 5.31 (5.33) (t, J = 2 Hz, 1H, Si–H), 7.06–7.29 (m, 4H, phenyl H)
7b,c	128–130	C, 61.01 (60.79); H, 5.46 (5.52)	1.47 (1.46) (d, J = 7 Hz, 3H, CH_3), 1.65–1.72 (m, 2H, CH_2), 3.27 (3.24) (hex, J = 7 Hz, 1H, CH), 5.39 (5.39) (t, J = 2 Hz, 1H, Si–H), 7.23–7.63 (m, 9H, phenyl H)
8a–c	136–138	C, 57.90 (57.72); H, 5.18 (5.40)	1.42 (1.41) (d, J = 7 Hz, 3H, CH_3), 1.58–1.78 (m, 2H, CH_2), 3.59 (3.19) (hex, J = 7 Hz, 1H, CH), 5.43 (5.35) (t, J = 2 Hz, 1H, Si–H), 6.87–7.40 (m, 9H, phenyl H)
9a–c	80–82	C, 45.58 (45.80); H, 4.67 (4.51)	1.42 (1.38) (d, J = 7 Hz, 3H, CH_3), 1.58–1.61 (m), 1.59 (dd, J = 2, 7 Hz, 2H, CH_2), 3.47 (3.17) (hex, J = 7 Hz, 1H, CH), 5.39 (5.31) (t, J = 2 Hz, 1H, Si–H), 6.97–7.27 (6.98–7.27) (m, 4H, phenyl H)
10a–c	104–106	C, 42.62 (42.68); H, 4.37 (4.71)	1.40, 1.39, and 1.38 (d, J = 7 Hz, 3H, CH_3), 1.58–1.61 (m), 1.60 (dd, J = 2, 7 Hz, 2H, CH_2), 3.73 and 3.16 (hex, J = 7 Hz, 1H, CH), 5.47, 5.37, and 5.34 (t, J = 2 Hz, 1H, Si–H), 7.13–7.35 (7.18–7.30) (d, J = 8 Hz, 4H, phenyl H)
11a–c	116–118	C, 36.27 (36.47); H, 3.72 (3.46)	1.40, 1.39, and 1.38 (d, J = 7 Hz, 3H, CH_3), 1.68–1.76, 1.59 (dd, J = 2, 7 Hz, 2H, CH_2), 3.71, 3.15, and 3.14 (hex, J = 7 Hz, 1H, CH), 5.49, 5.38, and 5.34 (t, J = 2 Hz, 1H, Si–H), 7.06–7.57 (7.12–7.45) (d, J = 8 Hz, 4H, phenyl H)
12	87–89	C, 53.44 (53.11); H, 6.52 (6.42)	1.36 (d, J = 7 Hz, 3H, CH_3), 1.55–1.72 (m, 2H, CH_2), 2.34 (s, 6H, CH_3), 3.42 (hex, J = 7 Hz, 1H, CH), 5.40 (t, J = 2 Hz, 1H, Si–H), 6.86–7.06 (m, 3H, phenyl H)
13ac,bb	91–93	C, 53.44 (53.12); H, 6.52 (6.42)	1.36 (1.39) (d, J = 7 Hz, 3H, CH_3), 1.55–1.73 (1.59–1.64) (m, 2H, CH_2), 2.32, 2.36 (2.33) (s, 3H (6H), CH_3), 3.42 (3.11) (hex, J = 7 Hz, 1H, CH), 5.39 (5.35) (t, J = Hz, 1H, Si–H), 7.00–7.17 (6.86–7.16) (m, 3H, phenyl H)
14ab,bc	96–98	C, 53.44 (54.18); H, 6.52 (6.59)	1.59–1.65 (m, 2H, CH_2), 1.40 (d, J = 7 Hz, 3H, CH_3), 2.27 (2.29) (s, 3H, CH_3), 3.14 (hex, J = 8 Hz, 1H, CH), 5.35 (t, J = 4 Hz, 1H, Si–H), 6.98–7.13 (m, 3H, phenyl H)
15ab,ba	115–118	C, 44.87 (44.51); H, 4.90 (4.51)	1.40 (1.39) (d, J = 7 Hz, 3H, CH_3), 1.56–1.72 (m, 2H, CH_2), 2.35 (2.34) (s, 3H, CH_3), 3.70 (3.41) (hex, J = 7 Hz, 1H, CH), 5.48 (5.44) (t, J = 2 Hz, 1H, Si–H), 6.95–7.27 (m, 3H, phenyl H)

[a] Distilled at 0.6 Torr.

bp 64–67 °C/0.6 mmHg) in 72% yield, and diadducts (0.6 g). For **3**: ^{1}H NMR δ 1.42 (d, J = 7 Hz, 3H, CH_3), 1.61–1.66 (m, 2H, CH_2), 3.19 (hex, J = 7 Hz, 1H, CH), 5.33 (t, J = 2 Hz, 1H, SiH), 7.22–7.37 (m, 5H, phenyl H); ^{13}C NMR δ 24.91 ($SiCH_2$), 30.37 (CH_3), 34.89 (CH), 126.51, 126.63, 128.68, 146.56 (phenyl carbons); Mass spectrum *m/e* (relative intensity) 222 (1), 220 (9), and 218 (14) (M^+), 177 (23), 175 (33), 105 (100), 103 (12), 99 (13), 91 (12), 78 (13), 77 (18), 63 (14). Anal. Calcd for $SiC_9H_{12}Cl_2$: C, 49.32; H, 5.52. Found: C, 49.26; H, 5.50.

The compounds **4–15** have been synthesized using the same methods describe above. The reaction data and product properties for the compounds are given in Tables 1 and 4, respectively.

Synthesis of 3-(Methylphenyl)-1-silabutane (4′a–c). To a diethyl ether solution of 8.2 g (35 mmol) of the mixture of **4a–c** described above was added a suspension of 103 mL of 1 M lithium aluminum hydride in tetrahydrofuran. The resulting mixture was stirred for 30 min and hydrolyzed. The organic layer was extracted with diethyl ether, washed with water, and dried over anhydrous magnesium sulfate. Vacuum distillation gave a mixture (bp 36–38 °C/0.6 mmHg) of 3-(*o*-, *m*-, and *p*-methylphenyl)-1-silabutanes (**4′a–c**; 5.6 g, 34 mmol) in 98% yield. For **4′a–c**: ^{1}H NMR δ 1.00–1.19 (overlapped peaks of **4′a–c**) (m, 2H, CH_2), 1.32, 1.31, and 1.32 (d, J = 7 Hz, 3H, CH_3), 2.33, 2.33, and 2.35 (s, 3H, CH_3), 3.17, 2.86, and 2.87 (hex, J = 7 Hz, 1H, CH), 3.44, 3.40, and 3.41 (t, J = 7 Hz, 1H, Si–H), 7.00–7.27 (overlapped peaks of **4′a–c**) (m, 4H, phenyl H); ^{13}C NMR δ 15.31, 16.11, and 16.11 ($SiCH_2$), 19.46, 21.48, and 20.98 (CH_3), 23.71, 24.45, and 24.63 (CH_3), 32.31, 37.28, and 37.61 (CH), 123.46, 124.96, 125.68, 126.25, 126.36, 126.80, 127.29, 128.25, 129.03, 130.23, 135.51 (overlapped phenyl carbons of **4′a–c**). Mass spectra for **4′a–c** were very similar: *m/e* (relative intensity) 164 (16) (M^+), 122 (43), 121 (66), 120 (16), 119 (100), 117 (30), 115 (26), 105 (28), 103 (11), 93 (14), 91 (69), 77 (25), 72 (12), 65 (19), 51 (12). Anal. Calcd for $SiC_{10}H_{16}$: C, 73.09; H, 9.81. Found for a mixture of three isomers (**4′a–c**): C, 73.22; H, 9.99.

Synthesis of 3-(2,5-Dimethylphenyl)-1-silabutane (12′). The reduction of **12** (2.4 g, 9.7 mmol) was carried out as described for the reduction of **4** with 1 M lithium aluminum hydride in tetrahydrofuran. Vacuum distillation gave 1.7 (9.5 mmol, bp 62–64 °C/0.6 mmHg) of **12′** in 97% yields: ^{1}H NMR δ 1.11–1.16 (m, 2H, CH_2), 1.29 (d, J = 7 Hz, 3H, CH_3), 2.29 and 2.32 (s, 3H, CH_3), 3.13 (hex, J = 7 Hz, 1H, CH), 3.44 (t, J = 3.5 Hz, 3H, 3H, Si–H), 6.89–7.04 (m, 3H, phenyl H); ^{13}C NMR δ 15.35 ($SiCH_2$), 19.35, 21.26, and 23.77 (CH_3), 32.44 (CH), 125.72, 126.50, 130.13, 131.92, 135.96, 146.15 (phenyl carbons). Mass spectrum: *m/e* (relative intensity) 178 (22) (M^+), 163 (10), 136 (31), 135 (55), 133 (100), 131 (20), 119 (15), 117 (18), 115 (22), 105 (38), 91 (27), 77 (14). Anal. Calcd for $SiC_{11}H_{18}$: C, 74.08; H, 10.17. Found: C, 74.21; H, 10.22.

Synthesis of 3-(Chloromethylphenyl)-1-silabutane (15′). The reduction of 3-(chloromethylphenyl)-1,1-dichloro-1-silabutane (3.7 g, 14 mmol) was carried out as described for the reduction of **4** with 1 M lithium aluminum hydride in tetrahydrofuran. Vacuum distillation gave 2.6 g (13 mmol, bp 50–52 °C/0.6 mmHg) of a mixture of both 3-(2-chloro-5-methylphenyl)-1-silabutane (**15′ab**; 80%) and 3-(5-chloro-2-methylphenyl)-1-silabutane (**15′ba**; 20%) in 93% yield. For **15′ab** (**15′ba**): ^{1}H NMR δ 1.10–1.27 (overlapped peaks of **15′ab** and **15′ba**) (m, 2H, CH_2), 1.33 (1.31) (d, J = 7 Hz, 3H, CH_3), 2.34 (2.31) (s, 3H, CH_3), 3.44 (3.13) (hex, J = 7 Hz, 1H, CH), 3.48 (3.47) (t, J = 4 Hz, 3H, Si-H), 6.93–7.27 (overlapped peaks of **15′ab** and **15′ba**) (m, 3H, phenyl H); ^{13}C NMR δ 14.86 (15.23) ($SiCH_2$), 221.06 (18.90) (CH_3), 22.79 (22.52) (CH_3), 33.05 (32.56) (CH), 125.29, 125.72, 127.51, 127.84, 129.16, 130.16, 131.51, 133.10, 136.66, 144.90, 148.36 (overlapped phenyl carbons of **15′ab** and **15′ba**). Mass spectra for both **15′ab** and **15′ba** were very similar: *m/e* (relative intensity) 200 (9) and 198 (26) (M^+), 157 (27), 156 (16), 155 (100), 154 (11), 153 (93), 145 (12), 121 (18), 119 (18), 117 (34), 116 (18), 115 (64), 105 (10), 93 (10), 92 (11), 91 (51), 89 (11), 77 (14), 65 (21), 63 (29). Anal. Calcd for $SiC_{10}H_{15}$: C, 60.42; H, 7.61. Found for a mixture of both **15′ab** and **15′ba**: C, 60.70; H, 7.89.

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Supplementary Material Available: Text giving ^{13}C NMR and mass spectral data for compounds **4–15** (4 pages). Ordering information is given on any current masthead page.

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