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Phosphonium Chloride-Catalyzed Dehydrochlorinative Coupling Reactions of Alkyl Halides with Hydridochlorosilanes

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The dehydrochlorinative Si−C coupling reactions of various primary and secondary alkyl chlorides with hydridochlorosilanes in the presence of tetrabutylphosphonium chloride as catalyst gave the coupling products with elimination of HCl as a gas. Coupling reactions of activated alkyl chlorides such as benzyl chlorides proceeded at 130 °C, while unactivated organic chlorides such as silylalkyl chlorides and secondary alkyl chlorides required higher reaction temperatures of 150 or 170 °C and longer reaction times. Primary alkyl chlorides reacted with trichlorosilane (**1**) to give coupling products in good to excellent yields, but secondary alkyl chlorides reacted at a slower rate and gave lower yields of products. Coupling reactions with methyldichlorosilane instead of **1** proceeded at slower rates and gave lower yields of products.

Introduction

Si−C bond forming reactions such as direct synthesis,[1] hydrosilylation,[2] and general organometallic reactions[3] are extremely important methods for the preparation of various organosilicon compounds and have been well-studied for a long time.[3] Another Si−C bond forming reaction, commonly known as the Benkeser reaction, is the dehydrochlorinative coupling of organic chlorides with trichlorosilane (**1a**).[4] A limitation of this reaction is that it is applicable only to activated organic halides[4] such as benzyl chloride[5] and allyl chloride,[6] and polyhalomethanes,[7] but not to unactivated alkyl chlorides such as butyl chloride.[4b] Furthermore, the reaction conditions require stoichiometric amounts of amine as an HCl scavenger, and all attempts to utilize methyldichlorosilane (**1b**) instead of **1a** as a coupling agent have been unsuccessful.

Recently, we studied the dehydrochlorinative reduction[8] of polychlorinated methylsilanes to monochloromethylsilanes to prepare starting materials for the direct synthesis of carbosilane compounds.[9−12] In this study, we found that organophosphines catalyzed the Si−C coupling reaction of alkyl chlorides with **1a**. After examining several different classes of phosphine compounds, we found that tetrabutylphosphonium chloride (TBPC) was the best catalyst for this novel, high-yielding dehydrohalogenative Si−C coupling reaction, and was required in only catalytic amounts.[13] This coupling reaction worked not only with activated organic chlorides, but also with unactivated organic chlorides such as cycloalkyl chlorides and silylalkyl chlorides. The coupling reaction of activated alkyl chlorides proceeded at 130 °C, while unactivated organic chlorides such as cycloalkyl chlorides and silylalkyl chlorides required higher reaction temperatures of 150 or 170 °C and longer reaction times.

Herein we wish to report the full details of the dehydrochlorinative Si−C coupling reactions of primary and secondary alkyl chlorides with hydridochlorosilanes **1a**,**b** in the presence of TBPC catalyst. In addition, we

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(1) (a) Rochow, E. G. *J. Am. Chem. Soc.* **1945**, *67*, 963. (b) Rochow, E. *Chemistry of Silicones*; Wiley: New York, 1951. (c) Petrov, A. D.; Mironov, B. F.; Ponomarenko, V. A.; Chernyshev, E. A. *Synthesis of Organosilicon Monomers*; Consultants Bureau: New York, 1964. (d) Lewis, K. M.; Rethwisch, D. G., Eds. *Catalyzed Direct Reactions of Silicon*; Elsevier: Amsterdam, The Netherlands, 1993.

(2) (a) Lukevitts, E. Y.; Voronkov, M. G. *Organic Insertion Reactions of Group IV Elements*; Consultants Bureau: New York, 1966. (b) Marciniec, B., Ed. *Comprehensive Handbook of Hydrosilylation*; Pergamon Press: New York, 1992; references therein. (c) Song, Y. S.; Yoo, B. R.; Lee, G.-H.; Jung, I. N. *Organometallics* **1999**, *18*, 3109.

(3) (a) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworth: London, 1981. (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983 (c) Rappoport, Z.; Apeloig, Y., Eds. *Chemistry of Organic Silicon Compounds*; John Wiley: New York, 1998. (d) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; John Wiley: New York, 2000.

(4) (a) Benkeser, R. A.; Gaul, J. M.; Smith, W. E. *J. Am. Chem. Soc.* **1969**, *91*, 3666. (b) Benkeser, R. A *Acc. Chem. Res.* **1971**, *4*, 94.

(5) Benkeser, R. A.; Foley, J. M.; Gaul, J. M.; Li, W. E.; Smith, W. E. *J. Am. Chem. Soc.* **1969**, *91*, 4578.

(6) Furuya, N.; Sukawa, T. *J. Organomet. Chem.* **1975**, *96*, C1.

(7) (a) Corriu, R. J. P.; Granier, M.; Lanneau, G. F. *J. Organomet. Chem.* **1998**, *562*, 79. (b) Benkeser, R. A.; Smith, W. E. *J. Am. Chem. Soc.* **1968**, *90*, 5307.

(8) Cho, Y. S.; Han, J. S.; Yoo, B. R.; Kang, S. O.; Jung, I. N. *Organometallics* **1998**, *17*, 570.

(9) Yeon, S. H.; Lee, B. W.; Kim, S.-I.; Jung, I. N. *Organometallics* **1993**, *12*, 4887.

(10) Jung, I. N.; Yeon, S. H.; Han, J. S. *Organometallics* **1993**, *12*, 2360.

(11) Lee, C. Y.; Han, J. S.; Oh, H. S.; Yoo, B. R.; Jung, I. N. *Bull. Korean Chem. Soc.* **2000**, 21, 1020.

(12) (a) Yeon, S. H.; Han, J. S.; Yoo, B. R.; Jung, I. N. *J. Organomet. Chem.* **1996**, *516*, 91. (b) Han, J. S.; Yeon, S. H.; Yoo, B. R.; Jung, I. N. *Organometallics* **1997**, *16*, 93.

(13) Cho, Y. S.; Kang, S.-H.; Han, J. S.; Yoo, B. R.; Jung, I. N. *J. Am. Chem. Soc.* **2001**, *123*, 5584.

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Table 1. Salt-Catalyzed Reactions of Benzyl Chlorides 2a−e (p-$XC_6H_4CH_2Cl$) with 1a[a]

entry no.	reactant **2**	catalyst	products **3** (%)[b]
1	**2a**, X = H	Bu_4PCl	**3a**[15] (95)[13]
2	**2b**, X = Cl	Bu_4PCl	**3b**[16] (94)
3	**2c**, X = F	Bu_4PCl	**3c**[17] (93)[13]
4	**2d**, X = Me	Bu_4PCl	**3d**[18] (95)
5	**2e**, X = MeO	Bu_4PCl	**3e**[19] (96)[13]
6	**2a**, X = H	Bu_4PBr	**3a** (85), $PhCH_3$ (9)
7	**2a**, X = H	Bu_4PI	**3a** (80), $PhCH_3$ (16)
8	**2a**, X = H	Bu_4NCl	**3a** (93)

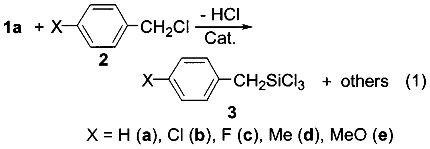
[a] Reactions were carried out at 130 °C for 4 h without solvent, using a 30:10:1 mol ratio of **1a** to **2** to catalyst. [b] Isolated yields.

propose a detailed mechanism for these reactions. These coupling reactions are new and useful for the synthesis of a wide range of functional organosilicon compounds.

Results and Discussion

A variety of activated and unactivated alkyl chlorides **2** reacted with hydridochlorosilanes **1a**,**b** in the presence of TBPC catalyst at reaction temperatures of 130−170 °C to afford the corresponding Si−C coupled compounds as major products through a dehydrochlorinative coupling reaction. In these reactions, 10 mol % catalyst with respect to **2** was used. Tetrabutylammonium chloride (TBAC) was also used as a catalyst and its activity was compared with that of TBPC. The reactivities of activated alkyl chlorides, such as benzyl chlorides and allyl chlorides, and unactivated alkyl chlorides[13] were also compared.

Reaction of *p*-Substituted Benzyl Chlorides with 1a. The Si−C coupling reactions of *p*-substituted benzyl chlorides **2a**−**e** with a 3-fold excess of **1a** in the presence of quaternary ammonium or phosphonium salts at 130 °C gave the corresponding benzyltrichlorosilanes **3a**−**e** in good yields (eq 1). An excess of **1a** was needed due to the disproportionation of **1a** to dichlorosilane and tetrachlorosilane under the reaction conditions.[14] The results obtained from these reactions under optimum conditions[13] are summarized in Table 1.



As shown in Table 1, coupling reactions of *p*-substituted benzyl chlorides **2a**−**e** with **1a** in the presence of TBPC catalyst at the relatively low temperature of 130 °C for 4 h gave the Si−C coupled products **3a**−**e** in excellent (93−96%) yields (entries 1−5). The reactions of benzyl chlorides **2a**−**e** with **1a** were monitored in 30 min time intervals by GLC. The production rates of **3a**−**e** and the yields were similar to each other, indicating that the para-substituent effect was not significant. When quaternary alkylphosphonium bromide or iodide was used as the catalyst instead of alkylphosphonium chloride for the reaction of **2a** with **1a**, the yields of **3a** slightly decreased and the amounts of toluene byproduct became detectable, indicating that the phosphonium chloride is the preferred catalyst (entries 1, 6, and 7). It is presently not clear whether the toluene byproduct was produced from a direct reduction of **2a** by **1a** or from the protodesilylation of **3a** by hydrogen chloride[20] under the reaction conditions.

Halide exchange reactions can also occur under certain conditions. When 10:1 mixtures of compound **2a** and tetrabutylphosphonium bromide and iodide were stirred at room temperature for 10 h, benzyl bromide (2%) and benzyl iodide (1%) were formed as minor products, respectively, through halide-exchange reactions between the chloro groups of **2a** and the halide of the quaternary salts. When benzyl bromide was reacted with **1a** at 130 °C for 10 h, benzyl chloride was produced resulting from halogen exchange between benzyl bromide and **1a**. The coupled product **3a** was obtained in 63% yield and toluene was obtained in 30% yield, suggesting that benzyl bromide is more easily reduced than benzyl chloride.

As mentioned previously, TBPC was the best catalyst among quaternary phosphonium halides in the Si−C coupling reaction of **2a** with **1a**. The same reaction with bulky tetraphenylphosphonium chloride as a catalyst afforded a lower yield of the major product **3a** (67%) and a higher yield of toluene (25%) as a byproduct. To compare the catalytic activities of tetrabutylammonium chloride (TBAC) and TBPC, the reaction of **2a** with **1a** was carried out in the presence of TBAC instead of TBPC. Product **3a** was obtained in excellent yield (93%) (entry 8), a rather surprising result since the same reaction with Et_4NCl as catalyst did not proceed.[13] It seems likely that the reactivity difference between the two ammonium salts may be related to solubility differences under our reaction conditions. Et_4NCl might be less soluble due to its smaller organic groups compared with TBAC and its higher melting point. In any event, these results indicate that TBAC is also an effective catalyst for the coupling reactions of benzyl chlorides.

To check the possibility of recycling the TBPC catalyst, the TBPC recovered from the reaction of **2a** with **1a** after bulb-to-bulb distillation of the product mixture was used for a second reaction. The reaction with the recycled TBPC catalyst under the same reaction conditions also gave **3a** in excellent yield (94%), indicating that the TBPC catalyst is reusable and stable at the reaction temperature. The unchanged nature of the recovered TBPC was also verified by NMR spectroscopy.

Salt-Catalyzed Reactions of Allyl Chlorides (2f−i) with 1a. The reactions of several allyl chlorides,

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(14) The disproportionation of **1a** in the presence of TBPC catalyst to dichlorosilane and tetrachlorosilane occurred slowly at room temperature and reached an equilibrium consisting of a 74:7:19 mixture of **1a**:dichlorosilane:tetrachlorosilane in GLC area percentage within 30 min at 150 °C.

(15) Schaefer, T.; Sebastian, R.; Penner, Glenn, H. *Can. J. Chem.* **1991**, *69*, 496.

(16) Schraml. J.; Chvalovsky, V.; Magi. M.; Lippmaa, E. *Collect. Czech. Chem. Commun.* **1975**, *40*, 897.

(17) Brook, A. G.; Kivisikk, R.; LeGrow, G. E. *Can. J. Chem.* **1965**, *43*, 1175.

(18) Chernyshev, E. A.; Komalenkova, N. G.; Bashkirova, S. A. *Zh. Obshch. Khim.* **1976**, *46* (6), 1286.

(19) Hiyashi, S.; Takashi, I.; Kazuo, N. *J. Appl. Polym. Sci.* **1992**, *44*, 1573.

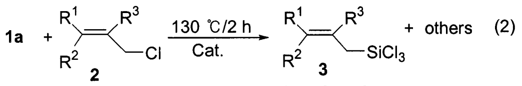
(20) The protiodesilylation of activated alkylsilanes such as allylsilanes and benzylsilanes is well-known. (a) Jenkins, P. R.; Gut, R.; Wetter, H.; Eschenmoser, A. *Helv. Chim. Acta* **1979**, *62*, 1922. (b) Fleming, I.; Marchi, D.; Patel, K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2518. (c) Yeon, S. H.; Lee, B. W.; Yoo, B. R.; Suk, M.-Y.; Jung, I. N. *Organometallics* **1995**, *14*, 2361. (d) Yoo, B. R.; Kim, J. H.; Lee, H.-J.; Lee, K.-B.; Jung, I. N. *J. Organomet. Chem.* **2000**, *605*, 239. (e) Jung, I. N.; Yoo, B. R. *Adv. Organomet. Chem.* **2001**, *46*, 145.

Table 2. Organic Salt-Catalyzed Reaction of Allyl Chlorides 2f−i [$R^1R^2C{=}C(R^3)CH_2Cl$] with 1a[a]

entry no.	reactant R^1	R^2	R^3	**2**	catalyst	products **3** (%)
9	H	H	H	**2f**	Bu_4PCl	**3f** (72), other (4)[b],
10	Me	H	H	**2g**	Bu_4PCl	**3g** (79)
11	H	H	Me	**2h**	Bu_4PCl	**3h** (78)
12	Me	Me	H	**2i**	Bu_4PCl	**3i** (90)
13	H	H	H	**2f**	Bu_4NCl	**3f** (48), others (26)[c]

[a] Reactions were carried out at 130 °C for 2 h. [b] 1,3-Bis(trichlorosilyl)propane[22a] was obtained as byproduct. [c] 1,3-Bis(trichlorosilyl)propane (12%) and propyltrichlorosilane[22b] (14%).

2f−i, with **la** were carried out in the presence of salts such as TBPC or TBAC. The corresponding allyltrichlorosilanes were obtained in good yields from TBPC-catalyzed reaction (eq 2). The results obtained from these Si−C coupling reactions under optimum conditions are summarized in Table 2.



$R^1 = R^2 = R^3 = H$ (**f**)
$R^1 = Me,\ R^2 = R^3 = H$ (**g**)
$R^1 = R^2 = H,\ R^3 = Me$ (**h**)
$R^1 = R^2 = Me,\ R^3 = H$ (**i**)

As shown in Table 2, the reactions of allyl chlorides **2f**−i with **1a** in the presence of TBPC at 130 °C for 2 h give allyltrichlorosilanes **3f−i** in good (72−90%) yields. The reaction of **2f** gave allyltrichlorosilane (**3f**,[6,21] 72%) and small amounts of 1,3-bis(trichlosilyl)propane (4%), formed by a coupling reaction followed by hydrosilylation with **1a** (entry 9). The reaction of methyl-substituted allyl chlorides such as crotyl chloride (**2g**), 2-methylallyl chloride (**2h**), and 1-chloro-3-methylbut-2-ene (**2i**) with **1a** gave crotyltrichlorosilane (**3g**)[21] in 79% yield, 2-methylallyltrichloroslane (**3h**)[21] in 78% yield, and 3-methylbut-2-enyltrichlorosilane (**3i**)[23] in 90% yield, respectively (entries 10−12). The reaction of **2f** with **1a** in the presence of TBAC catalyst instead of TBPC gave the coupled product **3f** in lower yield (48%) along with 1,3-bis(trichlosilyl)propane (12%) and propyltrichlorosilane (14%) as byproducts. The formation of propyltrichlorosilane may be explained by the protiodesilylation of 1,3-bis(trichlosilyl)propane by HCl. These results indicate that TBAC is a less effective catalyst than TBPC for these coupling reactions but promotes the hydrosilylation reaction of **2f** with **1a**[2b] and the protiodesilylation[20] of 1,3-bis(trichlosilyl)propane.

Reaction of Unactivated Chlorides and Silylalkyl Chlorides 2k−o with 1a. The Si−C coupling reactions of unactivated primary alkyl chlorides such as *n*-hexyl, octyl, decyl, and dodecyl chlorides with **1a** at 170 °C afforded the coupling products in excellent yields (92−94%).[13] As an example, *n*-hexyl chloride (**2j**) reacted with **1a** at 170 °C for 2 h to give hexyltrichlorosilane (**3j**) in 94% yield.[13] Silyl-substituted alkyl chlorides also underwent the Si−C coupling reaction with **1a** at 150 °C to give the corresponding coupled products, suggesting that silylalkyl chlorides are activated by silyl substituents.[13] To evaluate the substituent effect on the silicon of silylalkyl chlorides, the Si−C coupling reactions of silylalkyl chlorides [$Me_nCl_{3-n}Si(CH_2)_mCl$: $m = 1$, $n = 0$ (**2k**), 1 (**2l**), 2 (**2m**), 3 (**2n**); $m = 3$, $n = 3$ (**2o**)] with **1a** were carried out in the presence of TBPC catalyst at 150 °C. The coupled products **3k−o** were obtained in 91−94% yields (eq 3). The results are summarized in Table 3.

Table 3. Si−C Coupling Reaction of Silylalkyl Chlorides 2k−o [$Cl(CH_2)_mSiMe_nCl_{3-n}$] with 1a[a]

entry no.	reactant **2** m	n		reaction time (h)	product **3** (%)
14	1	0	**2k**	2	**3k**[24] (94)
15	1	1	**2l**	2.5	**3l**[25] (93)
16	1	2	**2m**	3	**3m**[25] (93)
17	1	3	**2n**	4.5	**3n**[26] (92)
18	3	3	**2o**	8	**3o**[27] (91)

[a] Reactions were carried out in the presence of TBPC at 150 °C.

$$\mathbf{1a} + \underset{\mathbf{2}}{Me_nCl_{3-n}Si(CH_2)_mCl} \xrightarrow[Bu_4PCl]{150\ ^\circ C} \underset{\mathbf{3}}{Me_nCl_{3-n}Si(CH_2)_mSiCl_3} \qquad (3)$$

m = 1, n = 0 (**k**); n = 1 (**l**); n = 2 (**m**); n = 3 (**n**)
m = 3, n = 3 (**o**)

As shown in Table 3, the yields of **3** were excellent. However, the reactions of silylmethyl chlorides (entries 14−17) were 2−4 times faster than that of (3-chloropropyl)trimethylsilane (entry 18), indicating that a silyl group nearer to the C−Cl bond facilitates the Si−C coupling reaction. This observation is also consistent with the higher reactivity of silyl-substituted alkyl chlorides compared to alkyl chloride. In the coupling reactions of (chloromethyl)silanes **2k−n** with **1a**, the reaction rate increased as the number of chloro groups on the silicon increased, indicating that electron-withdrawing groups on silicon facilitate the coupling reaction (entries 14−17).

Reactions of Secondary Alkyl Chlorides 2p−u with 1a. The TBPC-catalyzed coupling reactions were extended to secondary alkyl chlorides such as isoalkyl chlorides, cycloalkyl chlorides, 1-phenylethyl chloride (**2t**), and diphenylmethyl chloride (**2u**). Secondary alkyl chlorides **2p−u** reacted with **1a** at temperatures of 150−170 °C to give the coupled products **3p−u** in relatively low yields, and olefins as byproducts (eq 4). The results obtained from these reactions under optimum conditions are summarized in Table 4.

$$\mathbf{1a} + \underset{\mathbf{2}}{RCl} \xrightarrow[Bu_4PCl]{-\,HCl} \underset{\mathbf{3}}{RSiCl_3} + \text{others} \qquad (4)$$

R : ^{i}Pr (**p**), i-butyl (**q**), *c*-pentyl (**r**),
c-hexyl (**s**), PhMeCH (**t**), Ph_2CH (**u**)

As shown in Table 4, the coupling reactions of aliphatic alkyl chlorides (entries 19−22) required higher temperatures and longer times than phenyl-substituted alkyl chlorides (entries 23 and 24). The reaction of isopropyl chloride (**2p**) at 170 °C for 13 h afforded the coupled product **3p**[28] in good yield (76%) along with

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(21) Tsuji, J.; Hara, M.; Ohno, K. *Tetrahedron* **1974**, *30*, 2143.

(22) (a) Zhun', V. I.; Tsvetkov, A. L.; Bochkarev, V. N.; Slyusarenko, T. F.; Turkel'Taub, G. N.; Sheludyakov, V. D. *J. Gen. Chem. USSR* **1989**, *59*, 344. (b) Jenneskens, L. W.; Louwen, J. N.; Van den Berg, E. M. M.; Van Beuzekom, A. A.; Lugtenburg, J. *Recl. Trav. Chim. Pays-Bas* **1989**, *108*, 230.

(23) Benkerser, R. A.; Merritt, F. M., II; Roche, R. T. *J. Organomet. Chem.* **1978**, *156*, 235.

(24) Yeon, S. H.; Han, J. S.; Yoo, B. R.; Jung, I. N. *J. Organomet. Chem.* **1996**, *516*, 91.

(25) Deleris, G.; Birot, M.; Dungues, J.; Barbe, B.; Petraud, M.; Lefort, M. *J. Organomet. Chem.* **1984**, *266*, 1.

Table 4. Bu_4PCl-Catalyzed Reaction of Secondary Alkyl Chlorides 2p−u (R−Cl) with 1a

entry no.	reactant **2**	conditions		products (%)	
		temp (°C)	time (h)	**3**[a]	others
19	**2p**, R = *i*-Pr	170	13	**3p** (76)	propene (21)
20	**2q**, R = *i*-Bu	170	13	**3q** (39)	butene (57)
21	**2r**, R = *c*-pentyl	170	8	**3r** (22)	*c*-pentene (73)
22	**2s**, R = *c*-hexyl	170	8	**3s** (5)	*c*-hexene (91)
23	**2t**, R = PhMeCH	150	6	**3t** (35)	$PhCH_2CH_2SiCl_3$ (18), $PhCH_2CH_3$ (37)
24	**2u**, R = Ph_2CH	150	2	**3u** (21)	$(Ph)_2CHCH(Ph)_2$ (72), $(Ph)_2CH_2$ (5)

[a] Yields determined by GLC, using *n*-dodecane as an internal standard.

propene due to the dehydrochlorination of **2p** (entry 19). Under the same reaction conditions, isobutyl chloride (**2q**) afforded **3q**[29] in lower yield (39%) and a higher yield of butene as a byproduct (entry 20). The reaction of cyclopentyl chloride (**2r**) and cyclohexyl chloride (**2s**) with **1a** gave cyclopentyltrichlorosilane (**3r**)[30] and cyclohexyltrichlorosilane (**3s**)[28] in only 22% and 5% yields, respectively, along with cyclopentene and cyclohexene (entries 21 and 22). Overall, the Si−C coupling reactions of cycloalkyl chlorides are less favorable than reactions with noncyclic secondary alkyl chlorides.

The coupling reactions of secondary benzyl chlorides such as 1-phenylethyl chloride (**2t**) and diphenylmethyl chloride (**2u**) with **1a** took place at a slightly lower temperature (150 °C) than for secondary aliphatic alkyl chlorides **2p**−**s** (entries 23 and 24). The reaction of **2t** gave **3p**[31] in low yield (35%) along with 2-phenylethyltrichlorosilane (18%), and ethylbenzene (37%) as a hydrodechlorination product. In the case of **2u**, an unexpected product, 1,1,2,2-tetraphenylethane, was obtained as the major product in 72% yield, which may be explained by a C−C coupling reaction. These results suggest that C−C coupling reactions of phenyl-substituted secondary alkyl chlorides compete with Si−C coupling and become more favorable as phenyl substitution increases. (Diphenylmethyl)trichlorosilane (**3u**)[32] was formed in low yield (21%) in this reaction along with the hydrodechlorination product, diphenylmethane (5%).

In general, the reactions of primary alkyl chlorides with **1a** afforded coupling products in good to excellent yields, but secondary alkyl chlorides gave lower yields along with olefin byproducts due to dehydrochlorination of the starting secondary alkyl chlorides. Secondary alkyl chlorides required higher reaction temperatures and longer reaction times than primary chlorides, indicating that the reaction intermediate is sensitive to the steric bulk of the alkyl halides but not to the ease of carbocation formation.

Si−C Coupling Reactions of Alkyl Chlorides with 1b. The coupling reactions of activated alkyl chlorides **2a**, **2f**, and **2j** with methyldichlorosilane (**1b**) were studied in the presence of TBPC catalyst. These reactions required higher temperatures and longer reaction times and gave lower yields compared to the reactions with **1a**.[13] The results obtained from these reactions under optimum conditions are summarized in Table 5.

Table 5. Reaction of Activated Alkyl Chlorides 2 with 1b

entry no.	reactant **2**	conditions		products **3** (%)[a]
		temp (°C)	time (h)	
25	**2a**	150	10	**3a′** (49), $PhCH_3$ (49)
26	**2f**	150	8	**3f ′** (20)
27	**2j**	200	12	**3j′** (66)

[a] Yields determined by GLC, using *n*-dodecane as an internal standard.

As shown in Table 5, the reaction of **2a** with **1b** at 150 °C for 10 h gave benzyl(methyl)dichlorosilane (**3a′**)[33] in 49% yield and a 49% yield of toluene as a byproduct (entry 25). Reaction of **1b** with **2f** at 150 °C for 8 h gave allyl(methyl)dichlorosilane (**3f′**)[34] in low 20% yield (entry 26). The reaction of **2j** required a much higher temperature of 200 °C and gave hexyl(methyl)dichlorosilane (**3j′**)[35] in relatively good yield (66%) along with small amounts of unidentified products (entry 27). Although longer reaction times and higher temperatures are required, reactions with **1b** in place of **1a** give the corresponding coupling products in moderate yields.

When isopropyl chloride as a representative of secondary alkyl chloride reacted with **1b** at 180 °C for 4 h, an expected product of isopropylmethyldichlorosilane was not obtained in an appreciable amount, the decomposed products such as propene, propane, and hydrogen chloride were obtained instead.

Mechanism. On the basis of our results, we have proposed a mechanism for the TBPC-catalyzed dehydrohalogenative Si−C coupling reaction.[13] In the mechanism, the TBPC interacts with **1a** to form a pentacoordinated hydridotetrachlorosilane anion **I**[36] that loses hydrogen chloride on heating to give the tetraalkylphosphonium cation/trichlorosilyl anion pair **II**. Intermediate **II** subsequently attacks the alkyl chloride to produce the Si−C coupled product and regenerate the TBPC catalyst.[37, 38]

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(26) Nagaoka, S.-I.; Ohshita, J.; Ishikawa, M.; Takana, K.; Nagashima, U. *J. Chem. Phys.* **1995**, *102*, 6078.

(27) Topchiev, A. V.; Nametkin, N. S.; Chernysheva, T. I.; Durgaryan, S. G. *Dokl. Akad. Nauk., S.S.S.R.* **1965**, *100*, 97.

(28) Kaeppler, K.; Porzel, A.; Scheim, U.; Ruemann, K. *J. Organomet. Chem.* **1991**, *402*, 155.

(29) Dohmaru, T.; Nagata, Y. *J. Phys. Chem.* **1982**, *86*, 4522.

(30) Dohmaru, T.; Nagata, Y. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 1141.

(31) Fuji, K.; Sakurai, M.; Kinoshita, T.; Tada, T.; Kuroda, A.; Kawabata, T. *Chem. Pharm. Bull.* **1997**, *45*, 1524.

(32) Luh, L.-S.; Wen, Y.-S.; Tobita, H.; Ogino, H. *Bull. Chem. Soc. Jpn.* **1997**, 1997.

(33) Masumoto, H.; Kasahara, M.; Matsubara, I.; Takahashi, M.; Arai, T. *J. Organomet. Chem.* **1983**, *250*, 99.

(34) Marshall, R. L.; Young, D. J. *Tetrahedral Lett.* **1992**, *33*, 1365.

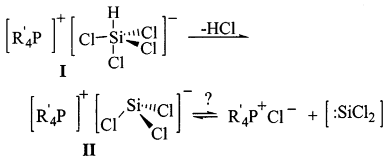
(35) Benouargha, A.; Boulahia, D.; Boutevin, B.; Caporiccio, G.; Guida-Pietrasanta, F.; Ratsimihety, A. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1996**, *113*, 79.

(36) See reviews for pentacoordinated organosilicon intermediates: (a) Prakash, G. K. S.; Yudin, A. K. *Chem. Rev.* **1997**, *97*, 757. (b) Corriu, R. J.; Colin, Y. J. *Chemistry of Organosilicon Compounds*; Patai, S., Rapporport, Z., Eds.; Wiley & Sons: New York; 1989; Vol. 2, p 1241.

(37) (a) Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. *Top. Curr. Chem.* **1986**, *131*, 99. (b) Patai, S.; Rapporport, Z., Eds. *The Chemistry of Organosilicon Compounds*; Wiley & Sons: New York, 1989; p 279.

(38) (a) Nozakura, S.; Konetsune, S. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 332. (b) Nozakura, S. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 660. (c) Nozakura, S. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 784.

Scheme 1



As an alternative, the coupled product can also be explained by insertion of dichlorosilylene, generated from trichlorosilyl anion by the loss of a chloride anion, into the C−Cl bond.[39] The trichlorosilyl anion has been postulated earlier,[40] and Benkeser reported NMR spectroscopic evidence for its existence in a mixture of tertiary amine and trichlorosilane.[4] However, he excluded the involvement of dichlorosilylene in his reactions, because he failed to trap the dichlorosilylene intermediate with diphenylacetylene.[4] Since the tetrabutylphosphonium chloride-catalyzed coupling reaction is different from the Benkeser reaction, it may not be reasonable to exclude the involvement of dichlorosilylene in this coupling reaction. The possibility of the formation of dichlorosilylene from trichlorosilyl anion still needs to be examined.Because of the electron-donating character of a methyl group, formation of pentacoordinated silyl anion intermediate ($MeCl_4Si^-$) generated by the reaction of **1b** with TBPC catalyst should be less favorable compared with HCl_4Si^- generated by the interaction of **1a** with TBPC. This may be the reason for the lower yields obtained from the reactions with **1b**.[36]

In conclusion, we describe a novel catalytic approach to the coupling of both primary and secondary alkyl chlorides with both trichlorosilane and methyldichlorosilane. A wide variety of organosilicon compounds can now be prepared easily in good yields by this method.

Experimental Section

General Comments. All reactions were carried out with flame-dried glassware or in a stainless steel bomb. All air-sensitive liquids were transferred by standard syringe or double tipped needle techniques.[41] Silane compounds such as trichlorosilane, methyldichlorosilane, (chloromethyl)trimethylsilane, (chloromethyl)dimethylchlorosilane, (chloromethyl)methyldiclorosilane, (chloromethyl)trichlorosilane, and (3-chloroproy)trimethylsilane were purchased from Gelest Inc and TCI. The (n-butyl)$_4$PCl, (n-butyl)$_4$PBr, (n-butyl)$_4$PI, n-dodecane, allyl chloride, methallyl chloride, crotyl chloride, n-hexyl chloride, benzyl chloride, p-flurobenzyl chloride, p-methoxybenzyl chloride, p-methylbenzyl chloride, p-chlorobenzyl chloride, isopropyl chloride, 2-chlorobutane, cyclopentyl chloride, cyclohexyl chloride, (1-chloroethyl)benzene, and chlorodiphenylmethane were obtained from Aldrich Chem. Co., Acros, and TCI. Reaction mixtures were analyzed by GLC over a 1.5 m by 1/8 in. stainless steel column packed with packing materials (10% SE-30 or SE-54 on 80−100 mesh Chromosorb P/AW) using a Varian 3300 gas chromatography equipped with a thermal conductivity detector and a Varian 4290 integrator. The progress of the reactions was monitored by GLC in time intervals of 30 min or 1 h. Samples for characterization were purified by preparative GLC using a Varian Aerograph series 1400 gas chromatograph with thermal conductivity detector and a 4 m by 1/8 in. stainless steel column packed with 15% SE-30 or SE-54. Product yields were determined by isolation or GLC with n-dodecane as the internal standard. Proton and carbon NMR spectra were recorded on a Bruker Avance 300 spectrometer (300 MHz for ^{1}H; 75 MHz for ^{13}C) with $CDCl_3$ 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 $CDCl_3$ 77.0 ppm (^{13}C). GC/MS data were obtained with a HP6890/5973 system (70 eV, EI). Measurements of recovered tetrabutylphosphonium bromide and iodide were analyzed by X-ray Fluorescence Spectroscopy (XRF, Rigagu RIX 2100 XRF, Japan) and were performed at a current of 60 mA and a voltage of 50 kV in technical vacuum with LiF(200) as analyzing crystal and scintillation counter as detector.

Coupling Reaction of 2a with 1a in the Presence of TBPC. Into a 25-mL stainless steel tube were added **2a** (2.00 g, 15.80 mmol), **1a** (6.45 g, 47.62 mmol), and TBPC (0.46 g, 1.56 mmol) under a dry nitrogen atmosphere. After the tube was sealed with a cap, the reaction mixture was heated at 130 °C for 4 h. After cooling, the reaction mixture was transferred to a 25-mL one-necked flask with a double-tipped needle. The mixture consisted of two layers of organic phase and catalyst. The reaction mixture was separated from the catalyst by bulb-to-bulb vacuum distillation and distilled to give **3a** (3.34 g; 140−2 °C/10 Torr) in 95% yield.

To test the catalytic ability of recycled TBPC, the TBPC catalyst remaining in the 25-mL tube was applied for the same reaction after the product **3a** and other volatiles obtained from the initial reaction above were removed by bulb-to-bulb distillation. The reaction with recycled TBPC gave **3a** (3.31 g) in excellent yield (94%). Data for **3a**: ^{1}H NMR ($CDCl_3$) δ 2.89 (s, 2H, $-CH_2-$), 7.17−7.33 (m, 5H, Ph-H); ^{13}C NMR δ 32.87 ($-CH_2-$), 126.47, 128.70, 129.21, 131.97 (Ph-C); mass spectrum, m/z (rel intensity) 224 (14, M$^+$), 133 (5, ($SiCl_3^+$)), 91 (100), 65 (17).

Coupling Reaction of 2b−e with 1a in the Presence of TBPC. Following the same procedure and scale described in the coupling reaction of **2a** with **1a** in the presence of TBPC (entries 2−5), the reactions of p-substituted benzyl chlorides **2b−e** with **1a** were carried out. These results are summarized in Table 1. Data for **3b**: ^{1}H NMR ($CDCl_3$) δ 2.91 (s, 2H, $-CH_2-$), 7.15−7.34 (q, 4H, Ph-H); ^{13}C NMR δ 32.25 ($-CH_2-$), 128.25, 128.93, 130.50, 132.54 (Ph-C); mass spectrum (70 eV, EI), m/z (rel intensity) 258 (15, M$^+$), 133 (6 ($SiCl_3$)$^+$), 127(41), 125(100), 89(23), 63 (17). Data for **3c**: ^{1}H NMR ($CDCl_3$) δ 2.91 (s, 2H, $-CH_2-$), 7.03−7.32 (m, 4H, Ph-H); ^{13}C NMR δ 31.97 ($-CH_2-$), 115.56, 115.85, 127.66, 130.62, 160.08, 163.33 (Ph-C); mass spectrum (70 eV, EI), m/z (rel intensity) 242 (12, M$^+$), 133 (4, ($SiCl_3$)$^+$), 109 (100), 83 (13), 63 (8), 57 (6). Data for **3d**: ^{1}H NMR ($CDCl_3$) δ 2.38 (s, 3H, Ph-CH_3), 2.92 (s, 2H, 3.83 $-CH_2-$), 7.13−7.20 (q, 4H, Ph-H); ^{13}C NMR δ 21.50 ($-CH_2-$), 32.87 (Ph-CH_3), 129.22, 129.57, 129.57, 136.62 (Ph-C); mass spectrum (70 eV EI), m/z (rel intensity) 238 (12, M$^+$), 133 (3, ($SiCl_3$)$^+$), 105 (100), 79 (7), 77 (11), 63 (4).

Study on Catalytic Activities of Tetrabutylphosphonium Halides for the Si−C Coupling Reaction. Following the same procedure and scale described in the coupling reaction of **2a** with **1a** in the presence of TBPC, tetrabutylphosphonium bromide and iodide instead of HBPC were applied to the Si−C coupling reactions, respectively (entries 6 and 7). With 5 min of stirring of a 1:3 mixture of **2a** and **1a** in the presence of tetrabuthylphosphonium bromide (10 mol % with respect to **2a**), benzyl bromide (1.7%) was detected by GLC with n-octadecane as an internal standard. The reaction mixture was kept at room temperature for 12 h and the composition remained the same. The coupling reaction of the

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[39] (a) Moser, D. F.; Bosse, T.; Olson, J.; Moser, J. L.; Guzei, I. A.; West, R. *J. Am. Chem. Soc.* **2002**, *124*, 4186. (b) Timms, P. L. *Inorg. Chem.* **1968**, *7*, 387.

[40] Nozakura, S.; Konotsune, S. *Bull. Chem. Soc. Jpn.* **1956**, *27*, 322.

[41] Shriver, D. F.; Drezdon, M. A. *Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

mixture was carried out at 130 °C for 4 h. The product mixture consisted of **3a** (85%) and toluene (8%) by GLC analysis. After the volatiles were distilled out, the residue was washed with dried *n*-hexane (3 × 5 mL) and dried to give white solids. XRF analysis of these solids showed a 99:1 mixture of tetrabutylphosphonium bromide and TBPC.

The same reaction with tetrabutylphosphonium iodide catalyst under the same conditions gave **3a** (80%) and toluene (16%). XRF analysis of the solids recovered after reaction showed a 99:1 mixture of tetrabutylphosphonium iodide and TBPC.

Coupling Reaction of 2a with 1a in the Presence of TBAC. Following the same procedure and mole scale described in the coupling reaction of **2a** with **1a** in the presence of TBPC, the reaction of **2a** with **1a** in the presence of 10 mol % TBAC (0.43 g, 1.56 mmol) at 130 °C for 4 h afforded **3a** (3.27 g) in 93% yield (entry 8).

Coupling Reaction of 2f with 1a in the Presence of TBPC. Following the same procedure described in the coupling reaction of **2a** with **1a** in the presence of TBPC, the reaction of **2f** (5.04 g, 65.86 mmol) with **1a** (26.77 g, 197.64 mmol) in the presence of TBPC (1.94 g, 6.58 mmol) at 130 °C for 2 h gave **3f** (8.32 g; 114 °C) in 72% yield and 1,3-bis(trichlorosilyl)propane (0.82 g; 115−7 °C/4 Torr) in 4% yield (entry 9). Data for 1,3-bis(trichlorosilyl)propane: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.59 (t, $J = 8.0$ Hz, d, $J = 5.4$, 4H, 2 ($\mathrm{SiC}H_2$)), 1.94 (m, 2H, $-\mathrm{C}H_2-$); ^{13}C NMR δ 16.41 ($\mathrm{Si}C\mathrm{H_2}$), 26.82 ($-C\mathrm{H_2}-$); mass spectrum (70 eV, EI), *m*/*e* (rel intensity) 308 (2, $\mathrm{M^+}$), 274 (69), 246 (22), 161 (59), 141 (28), 133 (100, $(\mathrm{SiCl_3})^+$), 125 (20), 71 (29), 63 (32), 57 (50).

Coupling Reaction of Methyl-Substituted Allyl Chlorides 3g−i with 1a in the Presence of TBPC. Following the same procedure described in the coupling reaction of **2f** with **1a** in the presence of TBPC, the reaction of methyl-substituted allyl chlorides **2g−i** with **1a** was carried out (entries 10−12). These results are summarized in Table 2.

Coupling Reaction of 2f with 1a in the Presence of TBAC. Following the same procedure and mole scale described in the coupling reaction of **2f** with **1a** in the presence of TBPC, the reaction of **2f** with **1a** in the presence of 10 mol % TBAC (1.83 g, 6.58 mmol) at 130 °C for 2 h afforded **3f** (5.55 g, 48%), 1,3-bis(trichlorosilyl)propane (2.46 g, 12%), and propyltrichlorosilane (1.64 g, 14%) (entry 13).

Coupling Reaction of Unactivated Chloromethylsilane 2k with 1a in the Presence of TBPC. Following the same procedure described in the coupling reaction of **2a** with **1a** in the presence of TBPC, the reaction of **2k** (3.00 g, 16.31 mmol) with **1b** (6.63 g, 48.95 mmol) in the presence of TBPC (0.48 g, 1.63 mmol) at 150 °C for 2 h gave **3k** (4.34 g; 183 °C) in 94% yield (entry 14).

Data for **3k**: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.87 (s, $\mathrm{SiC}H_2\mathrm{Si}$); ^{13}C NMR δ 22.42 ($\mathrm{Si}C\mathrm{H_2Si}$); mass spectrum (70 eV, EI), *m*/*z* (rel intensity) 247 (14, $((\mathrm{M} - \mathrm{Cl}) + 2)^+$), 213 (6), 133 (35, $(\mathrm{SiCl_3})^+$), 112 (100), 63 (72).

Coupling Reaction of Unactivated *ω*-Chloroalkylsilanes 2l−o with 1a in the Presence of TBPC. Following the same procedure described in the coupling reaction of **2k** with **1a** in the presence of TBPC, the reaction of *ω*-chloroalkylsilanes **2l−o** with **1a** was carried out (entries 15−17). These results are summarized in Table 3. Data for **3o**: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.02 (s, 9H, $\mathrm{C}H_3$), 0.63−0.69 (m, 2H, $(\mathrm{CH_3})_3\mathrm{SiC}H_2$), 1.44−1.49 (m, 2H, $-\mathrm{C}H_2-$), 1.57−1.66 (m, 2H, $\mathrm{C}H_2\mathrm{SiCl_3}$); ^{13}C NMR δ −1.72 ($-\mathrm{Si}(C\mathrm{H_3})_3$), 17.32 ($(\mathrm{CH_3})_3\mathrm{Si}C\mathrm{H_2}-$) 19.80 ($-C\mathrm{H_2}-$), 28.36 ($C\mathrm{H_2SiCl_3}$); mass spectrum (70 eV, EI), *m*/*z* (rel intensity) 233 (12, $(\mathrm{M} - \mathrm{CH_3})^+$), 133 (4, $(\mathrm{SiCl_3})^+$), 93 (13), 73 (100), 59 (17).

Coupling Reaction of Unactivated Secondary Alkyl Chloride 2p with 1a in the Presence of TBPC. Following the same procedure described in the coupling reaction of **2a** with **1a** in the presence of TBPC, the reaction of **2p** (3.04 g, 38.71 mmol) with **1a** (15.73 g, 116.13 mmol) in the presence of TBPC (1.12 g, 3.80 mmol) at 180 °C for 13 h gave **3p** (76% by GLC) and propene gas (entry 19).

Data for **3p**: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.18−1.20 (d, 6H, $(\mathrm{C}H_3)_2\mathrm{CH}$), 1.49−1.58 (m, $\mathrm{C}H\mathrm{SiCl_3}$); ^{13}C NMR δ 16.14 ($(C\mathrm{H_3})_2-$), 23.05 ($\mathrm{Cl_3Si}C\mathrm{H}$); mass spectrum (70 eV, EI), *m*/*z* (rel intensity) 176 (4, $\mathrm{M^+}$), 163 (23), 161 (23), 144 (13), 142 (69), 140 (100), 133 (69, $(\mathrm{SiCl_3})^+$), 125 (17), 112 (12), 98 (10), 63 (21).

Coupling Reaction of Secondary Alkyl Chlorides 2q−u with 1a in the Presence of TBPC. Following the same procedure described in the coupling reaction of **2p** with **1a** in the presence of TBPC, the reaction of other secondary alkyl chlorides **2q−u** with **1a** was carried out (entries 20−24). These results are summarized in Table 4.

Coupling Reaction of 2a with Methylsilane 1b in the Presence of TBPC. Following the same procedure described in the coupling reaction of **2a** with **1a** in the presence of TBPC, the reaction of **2a** (0.99 g, 7.82 mmol) and **1b** (2.70 g, 23.47 mmol) in the presence of TBPC (0.23 g, 0.78 mmol) at 150 °C for 10 h gave **3a′** (49% by GLC) and toluene (49%) (entry 25). Data for **3a′**: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.78 (s, 3H, $\mathrm{CH_2SiCl_2}CH_3$), 2.73 (s, 2H, Ph-CH_2Si), 7.20−7.36 (m, Ph-H); ^{13}C NMR δ 4.76 ($\mathrm{CH_2SiCl_2}C\mathrm{H_3}$), 31.42 ($\mathrm{Ph}C\mathrm{H_2Si}$), 126.29, 129.11, 129.32, 134.78 (Ph-C); mass spectrum (70 eV, EI), *m*/*z* (rel intensity) 204 (24, $\mathrm{M^+}$), 113 (34, $(\mathrm{Cl_2CH_3Si})^+$), 91 (100), 65 (17), 63 (12).

Coupling Reaction of Other Alkyl Chlorides 2f and 2j with 1b in the Presence of TBPC. Following the same procedure described in the coupling reaction of **2a** with **1b** in the presence of TBPC above, the reaction of other alkyl chlorides **2f** and **2j** with **1b** was carried out (entries 26 and 27). These results are summarized in Table 5.

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Supporting Information Available: NMR spectra for the compounds studied. This material is available free of charge via the Internet at http://pubs.acs.org.

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