Versatile Method for the Synthesis of Iodosilanes

Atsutaka Kunai,[*,1a] Tomohiro Sakurai,[1a] Eiji Toyoda,[1a] Mitsuo Ishikawa,[*,1a] and Yasushi Yamamoto[1b]

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 724, Japan, and Silicon-Electronics Materials Research Center, Shin-Etsu Chemical Co., Ltd., 1-10 Hitomi, Matsuida, Gunma 379-02, Japan

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A convenient method for the synthesis of alkyl- and phenyl-substituted iodosilanes has been reported. The reaction of triethylsilane with methyl iodide in the presence of a catalytic amount of palladium chloride at room temperature afforded Et_3SiI in 85% yield. Similarly, *n*-Bu_2MeSiI, *t*-$BuMe_2SiI$, Me_2PhSiI, $MePh_2SiI$, and Ph_3SiI were prepared in excellent yields, from the reaction of the respective monohydrosilanes with methyl iodide in the presence of the catalyst. The reaction of diethylsilane with methyl iodide gave Et_2SiI_2 and Et_2MeSiI in 37% and 20% yields. Similar reaction of diethylsilane with ethyl iodide produced Et_2SiI_2 and Et_3SiI in 31% and 36% yields, while with isopropyl iodide, diethylsilane afforded Et_2SiI_2 in 74% yield as the sole product. Diiodomethane, iodoform, and iodobenzene could be used as iodide sources.

Introduction

Organic iodosilanes have been shown to be useful reagents in organic synthesis. However, the synthesis of the iodosilanes, except for iodotrimethylsilane, has not been extensively studied. The method for the synthesis of iodotrimethylsilane reported to date involves the reaction of hexamethyldisilane,[2] trimethylphenylsilane,[3] allyltrimethylsilane,[4] and 1,4-bis(trimethylsilyl)cyclohexa-2,5-diene[5] with iodine and the reaction of chlorotrimethylsilane with sodium iodide in acetonitrile.[6] Organoiodosilanes other than iodotrimethylsilane have been prepared by methods involving cleavage of Ph—Si and H—Si bonds by iodine and hydrogen iodide,[7] of an Se—Si bond by iodine,[8] and of an N—Si bond by hydrogen iodide.[9] It has also been reported that the reaction of triorganosilanes with iodobenzene in the presence of a colloidal nickel catalyst at high temperature produces organoiodosilanes.[10]

During the course of our investigation concerning the synthesis of chlorosilanes from hydrosilanes in the presence of metal halides, we found that the reaction of hydrosilanes with iodocarbons in the presence of a catalytic amount of palladium chloride offers a convenient route to the iodosilanes with various substituents on the silicon atom.

Results and Discussion

Recently, we found that treatment of organohydrosilanes with 2 equiv of $CuCl_2$ in the presence of CuI in ether gave organochlorosilanes in high yields.[11] In an effort to extend this method to the synthesis of organoiodosilanes, we carried out the reaction of Et_3SiH with a small excess of iodine in the presence of CuI in benzene at room temperature. Et_3SiI was obtained in high yield. Similar CuI-catalyzed reaction of $PhMe_2SiH$ with iodine, however, produced $PhMe_2SiI$ only in low yield, because a Ph—Si bond is readily cleaved by the action of hydrogen iodide generated from the H/I exchange reaction. Moreover, the products were always contaminated with a trace of iodine. Therefore, we attempted to prepare the iodosilanes by a method that involves no elemental iodine and found that Si—H/C—I exchange readily takes place in the presence of a palladium chloride catalyst under mild conditions.

It is known that treatment of organohydrosilanes with chlorocarbons in the presence of a catalytic amount of palladium chloride afforded chlorosilanes in high yields.[12] We modified this method to be used for the synthesis of various types of the iodosilanes. Thus, the reaction of Et_3SiH with 1.8 equiv of methyl iodide in the presence of 0.5 mol % of palladium chloride at room temperature for 1.5 h afforded Et_3SiI in 85% isolated yield:

$$Et_3SiH + CH_3I \rightarrow Et_3SiI + CH_4$$

The reaction proceeded cleanly, and the product Et_3SiI could be readily isolated as a colorless liquid by simple distillation. No other products were detected in the distillate. Similar $PdCl_2$-catalyzed reaction of *n*-Bu_2MeSiH and *t*-$BuMe_2SiH$ with MeI produced *n*-Bu_2MeSiI and *t*-$BuMe_2SiI$ in 77% and 94% yields, respectively:

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$$n\text{-}Bu_2MeSiH + CH_3I \rightarrow n\text{-}Bu_2MeSiI + CH_4$$

$$t\text{-}BuMe_2SiH + CH_3I \rightarrow t\text{-}BuMe_2SiI + CH_4$$

The reaction conditions used and product yields are given in Table 1.

As can be seen in Table 1, the rate of Si—H/C—I exchange is quite slow at room temperature for the hydrosilanes bearing a bulky substituent on the silicon atom. However, a change in reaction temperature brings about a considerable reduction in time. For example, the reaction of *t*-BuMe$_2$SiH with MeI at room temperature requires 24 h for completion of the reaction, while at reflux temperature (bath temperature at 60 °C), the starting hydrosilane is completely consumed within 2.5 h. In these reactions, the formation of methane was verified by high-resolution mass spectrometric analysis of the gaseous product.

Interestingly, the present Si—H/C—I exchange reaction can be used for the synthesis of phenyl-substituted iodosilanes. Thus, the reaction of Me$_2$PhSiH with 2.2 equiv of MeI in the presence of 0.4 mol % of PdCl$_2$ at room temperature for 4 h gave Me$_2$PhSiI in 83% isolated yield. Similarly, the palladium-catalyzed reaction of MePh$_2$SiH with MeI produced MePh$_2$SiI in 91% isolated yield:

$$Me_2PhSiH + CH_3I \rightarrow Me_2PhSiI + CH_4$$

$$MePh_2SiH + CH_3I \rightarrow MePh_2SiI + CH_4$$

The reaction of Ph$_3$SiH with MeI is quite different from that of others described above. When the palladium catalyst was added to the mixture of Ph$_3$SiH and MeI in benzene,[13] the reaction proceeded smoothly, as indicated by evolution of methane. However, catalytic activities of PdCl$_2$ greatly decreased after several hours. When a trace of the catalyst was added to this mixture, the reaction proceeded again to produce Ph$_3$SiI. By adding the catalyst twice, finally Ph$_3$SiI was formed in 94% yield:

$$Ph_3SiH + CH_3I \rightarrow Ph_3SiI + CH_4$$

In all reactions, benzene and acetonitrile can be used as a solvent, as is seen in the above case, but the rate of the reaction becomes slow. Furthermore, diiodomethane, iodoform, and iodobenzene can also be used as iodide sources, although the reactivity of these iodides seems more sensitive to the substituents on a silicon atom than MeI. For example, the reaction of Me$_2$PhSiH with 2 equiv of PhI in the presence of 0.5 mol % of PdCl$_2$ at room temperature for 1 h yielded Me$_2$PhSiI in 91% isolated yield, while the reaction of MePh$_2$SiH with 1 equiv of PhI in the presence of 0.9 mol % of PdCl$_2$ at 60 °C (bath) for 4 h gave MePh$_2$SiI in 93% isolated yield. In contrast to these, the reaction of Et$_3$SiH (and also *t*-BuMe$_2$SiH) with PhI in the presence of 3 mol % of PdCl$_2$ is quite slow even at 80 °C. Most of the starting hydrosilane was recovered unchanged after 19 h of reaction time in this case.

The present method can be applied to the preparation of Et$_2$SiI$_2$ from Et$_2$SiH$_2$. When methyl iodide is used as the iodine source, a novel alkyl—hydrogen exchange reaction takes place along with the iodination reaction. Thus, when Et$_2$SiH$_2$ was treated with 3 equiv of MeI in the presence of 4 mol % of PdCl$_2$ at reflux temperature (60 °C) for 24 h, Et$_2$SiI$_2$ was obtained in 37% isolated yield, together with a 20% yield of Et$_2$MeSiI. The reaction of Et$_2$SiH$_2$ with 3 equiv of ethyl iodide in the presence of 0.9 mol % of PdCl$_2$ for 12 h led to a similar result. Again, not only Et$_2$SiI$_2$ but also Et$_3$SiI was obtained in 31% and 36% isolated yields, respectively:

$$Et_2SiH_2 + RI \rightarrow Et_2SiI_2 + Et_2RSiI + RH$$

$$R = CH_3,\ C_2H_5$$

In order to avoid the formation of trialkyliodosilanes, we tried to use a bulkier alkyl iodide. Thus, when Et$_2$SiH$_2$ was treated with 2.0 equiv of isopropyl iodide in the presence of 0.5 mol % of PdCl$_2$ at reflux temperature (bath 70 °C) for 24 h, the diiodosilane was formed as the sole volatile product. Distillation of the resulting solution afforded Et$_2$SiI$_2$ in 74% isolated yield:

$$Et_2SiH_2 + 2i\text{-}C_3H_7I \rightarrow Et_2SiI_2 + 2C_3H_8$$

In the reaction of diethylsilane with methyl iodide and ethyl iodide, disilanes and trisilanes were not detected in the reaction mixture, indicating that the production of Et$_2$MeSiI and Et$_3$SiI involves no diethylsilylene as a reactive intermediate.

A reasonable, although unproven, pathway for the formation of the products obtained is shown in Scheme 1. We propose the mechanism involving metathesis between an Si—Pd bond and a C—I bond. At the initial step, a silane adds oxidatively to the palladium catalyst to give an Si—Pd bond, and then the metathesis reaction between this bond and the iodo compound would take place, leading to the product.

The reaction of diethylsilane with alkyl iodide would produce diethyliodosilane, and the diethyliodosilane thus formed reacts again with the palladium catalyst to give a silyl—palladium complex. In the metathesis of the silyl—palladium complex with alkyl iodides, less hindered alkyl iodides such as methyl iodide and ethyl iodide give two types of products, diethyldiiodosilane and alkyldiethyliodosilane. In contrast, an alkyl iodide with a bulky substituent affords a single product, diethyldiiodosilane, because of steric hindrance.

At the initial stage of the reaction, metallic Pd would be produced from PdCl$_2$, since a hydrosilane is present in the solution. We assume that the metallic Pd thus formed serves as the active catalyst, as shown in Scheme 1. However, at present, we cannot rule out an alternative possibility that the alkyl iodide adds to the metal oxidatively to give a palladium complex such as Pd(SiR$_2$I)(R′)(H)(I), and then either R$_2$SiI$_2$ or R$_2$R′SiI is eliminated.

In conclusion, the palladium-catalyzed Si—H/R—I exchange reaction affords iodosilanes, especially aryl-substituted ones in high yields. The alkyl—hydrogen exchange reaction observed for diethylsilane may also offer a useful synthetic method for alkyldiethyliodosilanes.

Experimental Section

General Procedures. Benzene used as a solvent was dried over LiAlH$_4$ and distilled before use. Hydrosilanes were

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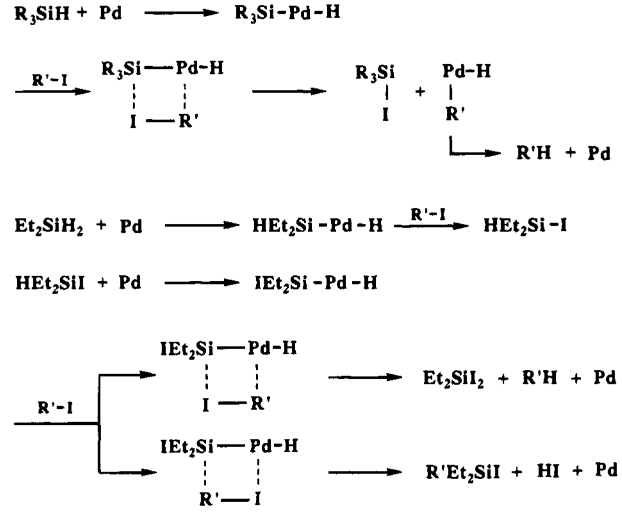
[13] In this reaction, Ph$_3$SiI is produced as a solid, and therefore the mixture becomes heterogeneous in the absence of the solvent.

Table 1. Reaction of Hydrosilanes with Iodocarbons

hydrosilane (amt, mmol)	iodocarbon (amt, mmol)	amt of PdCl$_2$, mol %	reacn time, h	bath temp, °C	iodosilane (yield, %)[a]
Et$_3$SiH (71.5)	CH$_3$I (130)	0.5	1.5	rt[f]	Et$_3$SiI (85)
Et$_3$SiH (40.3)	PhI (40.4)	3	19	80	Et$_3$SiI (low)[b]
n-Bu$_2$MeSiH (29.3)	CH$_3$I (67.6)	0.4	7	rt	*n*-Bu$_2$MeSiI (77)
t-BuMe$_2$SiH (104)	CH$_3$I (167)	0.3	24	rt	*t*-BuMe$_2$SiI (94)
t-BuMe$_2$SiH (71.4)	CH$_3$I (302)	0.9	2.5	60[c]	*t*-BuMe$_2$SiI (97)
Me$_2$PhSiH (73.6)	CH$_3$I (161)	0.4	4	rt	Me$_2$PhSiI (83)
Me$_2$PhSiH (71.4)	PhI (145)	0.5	1	rt	Me$_2$PhSiI (91)
MePh$_2$SiH (72.3)	CH$_3$I (141)	0.4	24	rt	MePh$_2$SiI (91)
MePh$_2$SiH (65.7)	CH$_3$I (282)	1	3	60[c]	MePh$_2$SiI (88)
MePh$_2$SiH (31.2)	PhI (31.6)	0.9	4	60	MePh$_2$SiI (93)
Ph$_3$SiH (70.8)	CH$_3$I (282)	2[d]	83	90[c,e]	Ph$_3$SiI (94)
Et$_2$SiH$_2$ (33.8)	CH$_3$I (102)	4	24	60[c]	Et$_2$SiI$_2$ (37) Et$_2$MeSiI (20)
Et$_2$SiH$_2$ (24.6)	C$_2$H$_5$I (73.9)	0.9	12	70[c]	Et$_2$SiI$_2$ (31) Et$_3$SiI (36)
Et$_2$SiH$_2$ (56.1)	*i*-C$_3$H$_7$I (115)	0.5	24	70[c]	Et$_2$SiI$_2$ (74)

[a] Yield of isolated product. [b] Conversion of hydrosilane was very low (GLC). [c] Under reflux conditions. [d] Catalyst was added portionwise. [e] Benzene (50 mL) was used as a solvent. [f] rt = room temperature.

Scheme 1



prepared by the reduction of the corresponding chlorosilanes with LiAlH$_4$. All iodination reactions of hydrosilanes were carried out under an atmosphere of dry nitrogen. Iodosilanes were isolated by distillation through a short distillation column. In all reactions with MeI, vigorous evolution of a gaseous product was observed. The presence of methane in a gas phase was verified by high-resolution GC−MS spectrometry. The results of the iodination reactions are summarized in Table 1. Representative experimental procedures are described below.

^{1}H and ^{13}C NMR spectra were determined with a JEOL Model EX-270 spectrometer using deuteriochloroform as a solvent. Mass spectra were measured on Shimadzu Model QP-1000 and Hitachi M-80B instruments. Iodosilanes were verified by comparing their physical and spectroscopic properties with those reported in the literature.[8-10,14-16] Analytical data for the iodination products are summarized in Table 2.

Table 2. Analytical Data for Iodosilanes

Me$_2$PhSiI:[14] bp 114−117 °C/17 mmHg; MS *m/e* 247 (M$^+$ − Me), 135 (M$^+$ − I); ^{1}H NMR (δ in CDCl$_3$) 1.04 (s, 6H, MeSi), 7.37−7.44 (m, 3H, phenyl ring H), 7.60−7.66 (m, 2H, phenyl ring H); ^{13}C NMR (δ in CDCl$_3$) 4.26 (MeSi), 128.07, 130.48, 133.33 (phenyl ring HC), 128.32 (ipso C)

MePh$_2$SiI:[10] bp 117−118 °C/1 mmHg; MS *m/e* 324 (M$^+$), 309 (M$^+$ − Me), 247 (M$^+$ − Ph), 197 (M$^+$ − I); ^{1}H NMR (δ in CDCl$_3$) 1.30 (s, 3H, MeSi), 7.39−7.44 (m, 6H, phenyl ring H), 7.65−7.68 (m, 4H, phenyl ring H); ^{13}C NMR (δ in CDCl$_3$) 3.33 (MeSi), 128.07, 130.57, 134.52 (phenyl ring HC), 133.93 (ipso C)

Et$_3$SiI:[8,9] bp 76−77 °C/20 mmHg; MS *m/e* 242 (M$^+$), 213 (M$^+$ − Et), 115 (M$^+$ − I); ^{1}H NMR (δ in CDCl$_3$) 1.01 (s, 15H, EtSi); ^{13}C NMR (δ in CDCl$_3$) 8.00, 8.54 (EtSi)

t-BuMe$_2$SiI:[8] mp 53−60 °C; MS *m/e* 242 (M$^+$), 185 (M$^+$ − *t*-Bu), 115 (M$^+$ − I); ^{1}H NMR (δ in CDCl$_3$) 0.70 (s, 9H, *t*-BuSi), 1.00 (s, 6H, MeSi); ^{13}C NMR (δ in CDCl$_3$) 1.10 (MeSi), 18.74, 25.63 (*t*-Bu)

Ph$_3$SiI:[15] bp 181−184 °C/1 mmHg; mp 150−155 °C; ^{1}H NMR (δ in CDCl$_3$) 7.39−7.45 (m, 9H, phenyl ring H), 7.64−7.67 (m, 6H, phenyl ring H); ^{13}C NMR (δ in CDCl$_3$) 128.05, 130.69, 135.74 (phenyl ring HC), 132.42 (ipso C)

n-Bu$_2$MeSi:[10] bp 120−125 °C/20 mmHg; MS *m/e* 227 (M$^+$ − Bu), 157 (M$^+$ − I); ^{1}H NMR (δ in CDCl$_3$) 0.72 (s, 3H, MeSi), 0.85−1.42 (m, 18H, *n*-BuSi), ^{13}C NMR (δ in CDCl$_3$) 1.89 (MeSi), 13.68, 18.56, 25.77, 26.40 (*n*-Bu)

Et$_2$SiI$_2$:[9] bp 180−185 °C, 89−91 °C/11 mmHg, 60−61 °C/1 mmHg; MS *m/e* 340 (M$^+$), 311 (M$^+$ − Et), 283 (HSiI$_2^+$), 213 (M$^+$ − I), 185 (EtHSiI$^+$), ^{1}H NMR (δ in CDCl$_3$) 1.07 (t, 6H, *J* = 7.7 Hz, SiCH$_2$C*H*$_3$), 1.56 (q, 4H, *J* = 7.7 Hz, SiC*H*$_2$CH$_3$); ^{13}C NMR (δ in CDCl$_3$) 8.72, 16.28 (EtSi)

Et$_2$MeSiI:[16] bp 75−80 °C/11 mmHg; MS *m/e* 228 (M$^+$), 199 (M$^+$ − Et), 101 (M$^+$ − I); ^{1}H NMR (δ in CDCl$_3$) 0.70 (s, 3H, MeSi), 1.00 (s, 10H, EtSi); ^{13}C NMR (δ in CDCl$_3$) 0.82 (MeSi), 7.89, 10.48 (EtSi)

Reaction of Triethylsilane with MeI. In a 50-mL flask fitted with a condenser was placed a mixture of 8.30 g (71.5 mmol) of Et$_3$SiH and 18.44 g (130 mmol) of MeI. Palladium chloride (59 mg, 0.33 mmol) was added, and the mixture was stirred by a magnetic stirrer at room temperature for 1.5 h. Excess MeI was distilled off, and the residue was fractionally distilled under reduced pressure to give 14.65 g (85% yield) of Et$_3$SiI as a colorless liquid, bp 76−77 °C/20 mmHg (lit.[8] bp 28−31 °C/0.05 mmHg; lit.[9] bp 191.5−192.5 °C/760 mmHg).

Reaction of *t*-Butyldimethylsilane with MeI. In a 50-mL flask fitted with a condenser was placed a mixture of 12.09 g (104 mmol) of *t*-BuMe$_2$SiH and 23.65 g (167 mmol) of MeI. Palladium chloride (59 mg, 0.33 mmol) was added, and the mixture was stirred by a magnetic stirrer at room temperature for 24 h. Excess MeI was distilled off, and the residue was sublimed under reduced pressure (5 mmHg) to give 23.6 g (94% yield) of *t*-BuMe$_2$SiI as colorless solids, mp 53−60 °C (lit.[8] mp 53−60 °C).

Reaction of Methyldiphenylsilane with PhI. In a 50-mL flask fitted with a condenser was placed a mixture of 6.18 g (31.2 mmol) of MePh$_2$SiH and 6.45 g (31.6 mmol) of

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iodobenzene. Palladium chloride (50 mg, 0.28 mmol) was added, and the mixture was heated at 60 °C (bath) with stirring for 4 h. The resulting mixture was fractionally distilled under reduced pressure to give 9.38 g (93% yield) of $MePh_2SiI$ as a colorless liquid, bp 117–118 °C/1 mmHg (lit.[10] bp 172.5–173.5 °C/5 mmHg).

Reaction of Triphenylsilane with MeI. To a solution of 18.41 g (70.8 mmol) of Ph_3SiH and 40.0 g (282 mmol) of MeI in 50 mL of benzene, placed in a 50-mL flask fitted with a condenser, was added 120 mg (0.68 mmol) of palladium chloride. The mixture was heated to reflux (bath 90 °C) with stirring for 83 h, during which time additional $PdCl_2$ was supplied twice (60 mg each). Excess MeI was distilled off, and the residue was fractionally distilled under reduced pressure to give 25.73 g (94% yield) of Ph_3SiI as a colorless solid: bp 181–184 °C/1 mmHg; mp 150–155 °C (lit.[15] mp 154–156 °C).

Reaction of Diethylsilane with MeI. To a mixture of 2.97 g (33.8 mmol) of Et_2SiH_2 and 14.5 g (102 mmol) of MeI, placed in a 50-mL flask fitted with a condenser, was added 250 mg (1.4 mmol) of palladium chloride. The mixture was heated to reflux (bath 60 °C) with stirring for 24 h. Excess MeI was distilled off, and the residue was fractionally distilled under atmospheric pressure to give 4.27 g (37% yield) of Et_2SiI_2 as a colorless liquid, bp 180–185 °C (lit.[9] bp 149–150 °C/102 mmHg). Redistillation of an earlier fraction afforded 1.54 g (20% yield) of Et_2MeSiI, bp 75–80 °C/11 mmHg (lit.[16] bp 161–166, 169 °C).

Reaction of Diethylsilane with EtI. To a mixture of 2.17 g (24.6 mmol) of Et_2SiH_2 and 11.5 g (73.9 mmol) of EtI, placed in a 50-mL flask fitted with a condenser, was added 40 mg (0.23 mmol) of palladium chloride. The mixture was heated to reflux (bath 70 °C) with stirring for 12 h. Excess EtI was distilled off, and the residue was fractionally distilled under reduced pressure to give 2.61 g of Et_2SiI_2 (31% yield) and 2.13 g of Et_3SiI (36%).

Reaction of Diethylsilane with *i*-PrI. To a mixture of 4.94 g (56.1 mmol) of Et_2SiH_2 and 19.6 g (115 mmol) of *i*-PrI, placed in a 50-mL flask fitted with a condenser, was added 50 mg (0.28 mmol) of palladium chloride. The mixture was heated to reflux (bath 70 °C) for 24 h. Excess *i*-PrI was distilled off, and the residue was fractionally distilled under reduced pressure to give 14.04 g (74% yield) of Et_2SiI_2 as a colorless liquid, bp 60–61 °C/1 mmHg.

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