Novel Phosphonium Chloride-Catalyzed Dehydrohalogenative Si−C Coupling Reaction of Alkyl Halides with Trichlorosilane

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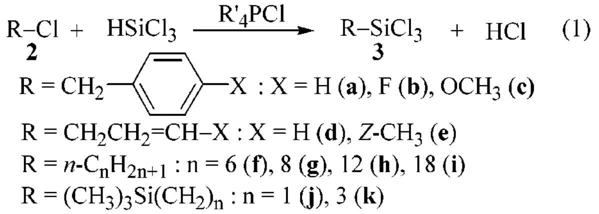
Si−C bond forming reactions such as the direct synthesis,[1] hydrosilylation,[2] and general organometallic reactions[3] are important methods for the preparation of various organosilicon compounds. Another established Si−C bond forming reaction is the coupling of activated organic chlorides with trichlorosilane (**1a**) commonly known as the Benkeser reaction.[4] Although this reaction generally proceeds in good yields, the reaction conditions require stoichiometric amounts of amine as an HCl scavenger. Furthermore, this reaction cannot be applied to unactivated alkyl chlorides such as butyl chloride,[4b] and all attempts to utilize methyldichlorosilane (**1b**) in place of **1a** as a coupling agent have been unsuccessful. In this report we wish to communicate our discovery of a novel high-yield approach to this reaction that requires only catalytic amounts of phosphonium salt in place of stoichiometric amounts of amine (eq 1). Moreover, the reaction



works effectively with unactivated chlorides and can further be extended to employ **1b** in the coupling step. As a whole, this chemistry will now enable the efficient, high-yield synthesis of a wide range of functionalized organosilicon compounds that were previously unavailable by simple means.

Table 1. Quaternary Organic Salt-Catalyzed Dehydrochlorinative Coupling Reaction of Organic Chlorides (**2**) with **1a**[a]

			conditions		
entry	**2**[b]	catalyst	temp (°C)	time (h)	products (%)[c] **3**
1	**2a** (−)	Et_3P	150	2	**3a** (88), other[d,e]
2	**2a** (−)	Bu_3P	150	2	**3a** (88), other[d,f]
3	**2a** (63)	Ph_3P	150	2	**3a** (12), others[d,g]
4	**2a** (68)	$^tBu_3P$	150	6	**3a** (11), others[d,h]
5	**2a** (−)	$(PhCH_2)Bu_3PCl$	150	2	**3a** (95)
6	**2a** (−)	Bu_4PCl	130	4	**3a** (95)
7	**2b** (−)	Bu_4PCl	130	4	**3b** (93)
8	**2c** (−)	Bu_4PCl	130	4	**3c** (96)
9	**2d** (−)	Bu_4PCl	130	2	**3d** (72), other[i]
10	**2e** (4)	Bu_4PCl	150	2	**3e** (79)
11	**2f** (−)	Bu_4PCl	170	2	**3f** (94)
12	**2g** (1)	Bu_4PCl	170	2	**3g** (94)
13	**2h** (−)	Bu_4PCl	170	4	**3h** (92)
14	**2i** (−)	Bu_4PCl	170	6	**3i** (93)
15	**2j** (1)	Bu_4PCl	150	4	**3j** (95)
16	**2k** (4)	Bu_4PCl	150	8	**3k** (91)
17	**2a** (−)	$(PhCH_2)Et_3NCl$	150	15	**3a** (47), other[j]
18	**2b** (11)	$(PhCH_2)Et_3NCl$	150	15	**3b** (49), other[k]
19	**2c** (6)	$(PhCH_2)Et_3NCl$	150	15	**3c** (54), other[l]
20	**2f** (100)	Et_4NCl	200	6	**3f** (−)

[a] The reactions were carried out using a 30:10:1 mole ratio of **1a** to **2** to catalyst. [b] Unreacted **2** in parentheses. [c] The isolated yields unless otherwise noted. [d] Yields determined by GLC using *n*-dodecane as an internal standard. [e] $(PhCH_2)Et_3PCl$ (10%) was obtained. [f] $(PhCH_2)Bu_3PCl$ (10%). [g] $(PhCH_2)Ph_3PCl$ (10%) and toluene (20%). [h] $(PhCH_2)^tBu_3PCl$ (10%) and toluene (20%) as byproducts. [i] $Cl_3Si(CH_2)_3SiCl_3$ (4%). [j] Toluene (50%). [k] *p*-Fluorotoluene (29%). [l] *p*-Methoxytoluene (33%).

Recently, we have reported the successful extension of Rochow's direct synthesis reaction to include a variety of organic[5] and organosilyl[6] chloride compounds in place of chloromethane. To prepare starting materials such as (chloromethyl)silanes and (dichloromethyl)silanes for these reactions,[7] we investigated the selective reduction of polychlorinated methylsilanes with **1a** in the presence of catalytic amounts of group 10 transition metal compounds.[8] In our studies, we found that small amounts of dehydrochlorinative Si−C coupling products of (chloromethyl)-silane were obtained as byproduct when triphenylphosphine (TPP)−metal complexes were used as catalysts.[9] Speculating that dissociated TPP was involved in this coupling reaction, we reacted benzyl chloride (**2a**) with **1a** at 150 °C in the presence of 10 mol % of various triorganophosphines (Table 1, entries 1−4). Excess amounts of **1a** were employed to favor the formation of products.

As shown in Table 1, reaction of **1a** with **2a** in the presence of triethylphosphine or tributylphosphine at 150 °C for 2 h (entries 1 and 2) gave in both cases the coupling product **3a** in 88% isolated yield and 10% of the corresponding benzyltrialkylphosphonium chlorides, a result of the coupling of the trialkylphosphines with **2a**.[10] However, **3a** was obtained in only 12 or 11% yields with toluene as the major product when TPP or tri(*tert*-butyl)phosphine was employed, respectively (entries 3 and 4). It

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(9) The 1:5 reaction of (trimethylsilyl)methyl chloride (**2j**) with **1** in the presence of tetrakis(triphenylphosphine)palladium under the same conditions of the reductive hydrodechlorination previously reported[8] gave [(trimethylsilyl)-methyl]trichlorosilane (**3j**) in 1% yield, based on **2j** used, as a byproduct. In a later study we found that (silylmethyl)triphenylphosphonium chloride, formed from the reaction of **2j** with triphenylphosphine dissociated from the palladium complex, catalyzed this reaction, even though the coupling product **3j** was obtained in low yield.

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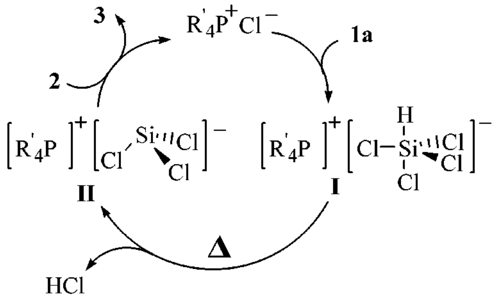
is not presently clear whether toluene was produced by a direct reduction of **2a** by **1a** or by the desilylation of **3a** by HCl.[11] However, these reactions at least demonstrate that sterically bulky catalysts are less active and enhance the reduction or desilylation reaction. The presence of the phosphonium salts in the reactions also suggested to us that the trialkylphosphines might not be the catalysts but rather the phosphonium salts. Accordingly, the same coupling reactions using tetrabutylphosphonium chloride (TBPC) or benzyltributylphosphonium chloride as a catalyst gave **3a** in near quantitative yields within 4 h (entries 5 and 6), confirming that the quaternary phosphonium chlorides were indeed the catalysts for the Si−C coupling reaction.

Once we had determined that phosphonium salts were the catalysts for this reaction, we examined the reactions of various organic chlorides with **1a**.[12] The reactions of para-substituted benzyl chlorides **2a**−**c** at the slightly lower temperature of 130 °C gave products **3a**−**c** in 93−95% isolated yields (entries 6−8). Allyl chloride (**2d**) reacted with **1a** to give **3d** in moderate yield (72%) along with 1,3-bis(trichlorosilyl)propane (**4**, 4%) as the byproduct (entry 9). **4** was likely obtained by the hydrosilylation of **3d** with **1a**.[13] The reaction with crotyl chloride (**2e**) at 130 °C gave **3e** in good yield (79%) without any hydrosilylation product (entry 10). Of particular significance is the extension of the coupling reaction to unactivated *n*-alkyl chlorides; simple chlorides [$C_nH_{2n+1}Cl$: $n = 6$ (**2f**), 8 (**2g**), 12 (**2h**), 18 (**2i**)] and *ω*-(trimethylsilyl)alkyl chlorides [alkyl = methyl (**2j**), propyl (**2k**)] were reacted with **1a** at 170 °C. In 2−6 h reactions, products **3f**−**i** were obtained in excellent yields (92−94%) (entries 11−14), and in 4−8 h reactions, products **3j** and **3k** were obtained in 91 and 95% yields, respectively. We found that in general the coupling reactivity of the *n*-alkyl chlorides decreased as the chain length of the alkyl group increased. In the case of *ω*-(trimethylsilyl)alkyl chlorides, the reactivity of **2j** at 150 °C was higher than that of **2k**, possibly indicating that the electron-donating effect of the silyl group facilitated the Si−C coupling reaction. Bromoorganic compounds could also be utilized in this coupling reaction, although side products were more evident. As an example, **1a** was reacted with benzyl bromide for 10 h at 130 °C in the presence of TBPC catalyst. The coupling product **3a** was obtained in 63% yield with a 37% recovery of toluene as a byproduct. Compounds such as bromotrichlorosilane and bromodichlorosilane, resulting from bromine−chlorine exchange, were also obtained in this reaction.

Scheme 1



Compared to the phosphonium salts, quaternary organoammonium chlorides were found to be less effective catalysts for the coupling reaction. Reactions of benzyl chlorides **2a**−**c** with **1a** in the presence of 10% benzyltriethylammonium chloride using the phosphonium salts-catalyzed reaction conditions gave products **3a, 3b,** and **3c** in 47, 49, and 54% yields and the corresponding methylbenzene compounds in 50, 29, and 33% yields at 150 °C for 15 h, respectively (entries 17−19). Reactions with nonactivated alkyl chlorides **2f**−**k** using quaternary ammonium chloride catalysts gave no coupling products up to a reaction temperature of 200 °C but instead gave the reductive dealkylation products of quaternary ammonium chloride (entry 20).

Although requiring slightly higher temperatures and reaction times, reactions with **1b** in place of **1a** give the corresponding coupled products in respectable yields. In the presence of TBPC catalyst, reaction of **1b** with **2a** for 10 h at 130 °C gave benzyl(methyl)dichlorosilane in 50% yield and 50% toluene as a byproduct. In a similar reaction with **2f** for 12 h at 200 °C, 91% of **2f** was consumed to give hexyl(methyl)dichlorosilane (66%) with smaller amounts of unidentified products.

The mechanism proposed by Benkeser[4b] is not appropriate for our system. On the basis of our results, we propose a plausible mechanism for the TBPC-catalyzed dehydrohalogenative Si−C coupling reaction as shown in Scheme 1. In this mechanism, the TBPC interacts with **1a** to form a pentacoordinated hydridotetrachlorosilane anion **I**[14] which loses hydrogen chloride upon heating to give the tetraalkylphosphonium cation/trichlorosilyl anion pair **II**. Intermediate **II** subsequently attacks the alkyl chloride to produce the Si−C coupling product and regenerate the TBPC catalyst.[15,16]

In conclusion, we describe a novel catalytic approach to the coupling of both activated and nonactivated alkyl halides with both trichlorosilane and methyldichlorosilane. A wide variety of silyl-functionalized compounds may now be prepared easily and in good yields. The extension of the coupling reaction to other alkyl halides such as secondary and tertiary alkyl halides is currently being investigated.

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[12] As a representative reaction, the reaction of **2a** with **1** is described as follows: A 25 mL dried stainless steel bomb equipped with a valve was charged with TBPC (0.22 g, 0.75 mmol), **2a** (0.95 g, 7.5 mmol), and **1** (3.41 g, 25.2 mmol) under a dry nitrogen atmosphere. After the valve was closed, the reactor was kept in an oil bath at 130 °C for 4 h. The reaction mixture was fractionally distilled to give **3a** (1.61 g, 7.1 mmol) in 95% yield. TBPC remained as a residue in the bomb after distillation, as confirmed by the analysis of NMR data.

[13] The Bu_4PCl-catalyzed hydrosilylation of **3d** with **1** at 130 °C for 2 h gave product **4** in low yield (2%).

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