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Si–C coupling reaction of polychloromethanes with $HSiCl_3$ in the presence of Bu_4PCl: Convenient synthetic method for bis(chlorosilyl)methanes

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Abstract

Coupling reaction of polychloromethanes $CH_{4-n}Cl_n$ ($n = 2$–4) with $HSiCl_3$ in the presence of tetrabutylphosphonium chloride (Bu_4PCl) as a catalyst occurred at temperatures ranging from 30 °C to 150 °C. The reactivity of polychloromethanes increases as the number of chlorine-substituents on the carbon increases. In the reactions of CCl_4 with $HSiCl_3$, a variety of coupling products such as bis(chlorosilyl)methanes $CH_2(SiCl_3)(SiXCl_2)$ [X = Cl (**1a**), H (**1b**)], (chlorosilyl)trichloromthanes $Cl_3CSiXCl_2$ [X = Cl (**2a**), H (**2b**)], and (chlorosilyl)dichloromthanes $Cl_2HCSiXCl_2$ [X = Cl (**3a**), H (**3b**)] were obtained along with reductive dechlorination products such as $CHCl_3$ and CH_2Cl_2 depending on the reaction temperature. In the reaction of CCl_4, **2a** is formed at the initial stage of the coupling reaction and converted to give $CHCl_3$ at low temperature of 30 °C, to give **1a**, **3a**, and $CHCl_3$ at 60 °C, and to afford **1a** as major product and CH_2Cl_2 in competition above 100 °C. Si–H bond containing silylmethanes can be formed by the H–Cl exchange reaction with $HSiCl_3$. Reaction of $CHCl_3$ with $HSiCl_3$ took placed at 80 °C to give three compounds **1a**, **3a**, and CH_2Cl_2, and finally **3a** was converted to give **1a** and CH_2Cl_2 at longer reaction time. While the condition for the reaction of CH_2Cl_2 with $HSiCl_3$ required a much higher temperature of 150 °C. Under the optimized conditions for synthesizing bis(chlorosilyl)methanes **1a**,**b**, a mixture of **1a** and **1b** were obtained as major products in 65% (**1a**:**1b** = 64:1) and 47% (42:5) yields from the reaction of CCl_4 and $CHCl_3$ at 100 °C for 8 h, respectively, and in 41% (34:7) yield from that of CH_2Cl_2 at 170 °C for 12 h. In the Si–C coupling reaction of polychloromethanes with $HSiCl_3$, it seems likely that a trichlorosilyl anion generated from the reaction of $HSiCl_3$ with Bu_4PCl is an important key intermediate.

Keywords: Tetrachloromethane; Chloroform; Methylene chloride; Bis(chlorosilyl)methane; Trichlorosilane; Si–C coupling

1. Introduction

Trichlorosilane ($HSiCl_3$) undergoes a variety of interesting and useful Si–C bond formation reactions with organometallic reagents [1] and unsaturated organic compounds in the presence of transition metal complexes [2] to give various organosilanes containing Si–Cl bonds as functionalities, which are used as important starting materials in the silicones industry [3]. Another established Si–C bond forming method is the organic base-catalyzed reaction of activated alkyl chlorides such as benzyl chloride and polychlromethane with $HSiCl_3$ [4]. Tertiary amines catalyze the coupling reaction of activated polychloromethanes [4] such as chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4) [5] with $HSiCl_3$ affording bis(chlorosilyl)methanes in moderate yields, respectively. Recently, we have reported successful coupling reactions with organic chlorides affording alkyltrichlorosilanes in high yields in the presence of quaternary phosphonium chloride as a catalyst in place of amine [6,7], the introduction of $SiCl_2$ moiety to butadienes to form 1,1-dichlorosilacyclopent-3-enes [8], and the double silylation

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of olefins with $HSiCl_3$ to produce α,β-(trichlorosilyl)alkanes as major products [9]. In the coupling reaction of primary alkyl chlorides, their reactivity depends on the substituents at the carbon of C–Cl. The reaction of activated alkyl chlorides such as allyl chlorides and benzyl chlorides occurs at 130 °C, but those of unactivated alkyl chlorides such as 1-hexyl chloride and 1-octyl chloride require the high temperature of 170 °C [7]. The success of these coupling reactions prompted us to extend this reaction to polychloromethanes $CH_{4-n}Cl_n$ ($n = 2$–4), which are expected to react with $HSiCl_3$ to yield poly(silyl)methanes as coupling products. The reaction of polychloromethanes with $HSiCl_3$ in the presence of Bu_4PCl occurred at the temperatures ranging from 30 °C to 150 °C depending on chlorine-substituents on the carbon to give a variety of Si–C coupling products and reductive dechlorination compounds. Herein, we wish to report the Bu_4PCl-catalyzed reaction of polychloromethanes with $HSiCl_3$ and a mechanism for the formation of Si–C coupling compounds in details.

2. Results and discussion

2.1. Reaction of CCl_4 with $HSiCl_3$

When the most activated CCl_4 among the polychloromethanes reacted with $HSiCl_3$, a variety of coupling products such as bis(chlorosilyl)methanes $CH_2(SiCl_3)(SiXCl_2)$ [X = Cl (**1a**), H (**1b**)], (chlorosilyl)trichloromethanes $Cl_3CSiXCl_2$ [X = Cl (**2a**), H (**2b**)], and (chlorosilyl)dichloromethanes $Cl_2HCSiXCl_2$ [X = Cl (**3a**), H (**3b**)] were obtained along with reductive dechlorination products such as $CHCl_3$ and CH_2Cl_2 depending on the reaction temperatures (Eq. (1)). Si–H bond containing silylmethanes (**1b**–**3b**) can be formed by the H–Cl exchange reaction with $HSiCl_3$. The results obtained from the reactions of CCl_4 with $HSiCl_3$ at temperatures ranging from 30 °C to 130 °C are summarized in Table 1.

As shown in Table 1, the reaction of CCl_4 with $HSiCl_3$ occurred at 30 °C and gave a coupling product **2a** (3%) and a reductive dechlorination product $CHCl_3$ (42%) as a major product with a 45% consumption of CCl_4 for 8 h (entry 1). At the higher temperature of 60 °C, a 4 h reaction gave a 76% consumption of CCl_4 and afforded a 3:2 mixture of **2a** and **2b** and $CHCl_3$ in 48% and 27% yields, respectively, (entry 2) and an 8 h reaction with all consumption of CCl_4 gave a 15:1 mixture of **1a** and **1b**, a 15:1 mixture of **2a** and **2b**, and a 12:1 mixture of **3a** and **3b** in 16%, 16% and 13% yields, respectively, as well as $CHCl_3$ in 53% yield (entry 3). When the same reaction was carried out at the temperature of 80 °C, all CCl_4 was consumed within 2 h to give a 34:3 mixture of **1a** and **1b** and a 14:1 mixture of **3a** and **3b** in 37% and 15% yields along with reductive dechlorination products such as $CHCl_3$ (47%) and CH_2Cl_2 (1%) (entry 4). In a longer 8 h reaction at 80 °C, the yield of compounds **1** consisted of a 51:3 mixture of **1a** and **1b** increased up to 54% along with CH_2Cl_2 (11%), but that of $CHCl_3$ decreased to 31%, suggesting that the coupling reaction of $CHCl_3$ with $HSiCl_3$ takes place at 80 °C (entry 5). The yield of a mixture of **1** was maximized to 69% in an 8 h reaction at 100 °C (entry 6) and then decreased to 53% in a 1 h reaction at a higher temperature of 130 °C (entry 7). When $HSiMeCl_2$ was used as a hydrosilane instead of $HSiCl_3$, no Si–C coupling reaction with CCl_4 even at 80 °C was observed. In the reaction of CCl_4 with $HSiCl_3$, the coupling product **2a** formed at the beginning stage is an important intermediate leading to silylmethanes **3** and $CHCl_3$ (entries 2 and 3), and finally to bis-silylation products **1**.

2.2. Reaction of Cl_3SiCCl_3 (**2a**) with $HSiCl_3$

In order to look into the reaction pathway to **1** from CCl_4, monosilylated compounds **2a**, formed at the early

$$CCl_4 + HSiCl_3 \xrightarrow[HCl]{} \underset{\mathbf{1}}{Cl_3Si{-}CH_2{-}SiXCl_2} + \underset{\mathbf{2}}{Cl_2XSi{-}CCl_3} + \underset{\mathbf{3}}{Cl_2XSi{-}CHCl_2} + CHCl_3 + CH_2Cl_2 \quad (1)$$

X = Cl (**a**), H (**b**)

Table 1
Bu_4PCl-catalyzed reactions of CCl_4 with $HSiCl_3$[a]

Entry #	CCl_4[b]	Reaction conditions		Product yields (%)[c]				
		Temperature (°C)	Time (h)	**1** (**a**:**b**)	**2** (**a**:**b**)	**3** (**a**:**b**)	$CHCl_3$	CH_2Cl_2
1	55	30	8	–	3(3:–)		42	
2	24	60	4	–	48 (29:19)		27	
3		60	8	16 (15:1)	16 (15:1)	13 (12:1)	53	
4		80	2	37 (34:3)	–	15 (14:1)	47	1
5		80	8	54 (51:3)	–	3 (3:–)	31	11
6		100	8	69 (67:2)	–		–	30
7		130	1	53 (52:1)	–		–	33

[a] The reaction was carried out using a 10:60:1 mol ratio of CCl_4, $HSiCl_3$, and Bu_4PCl.
[b] Unreacted CCl_4 (%) remained.
[c] Yields are on the basis of CCl_4 used and were determined by GLC with use of internal standard.