One-Pot Transformation of RCHO to (*E*)-RCH=CHSiMe$_3$ Using CHI$_3$, Mn, Me$_3$SiCl, and a Catalytic Amount of CrCl$_2$

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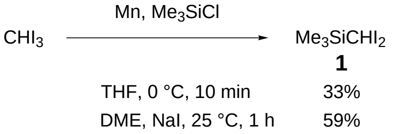
Abstract: Iodoform is reduced with manganese in the presence of Me$_3$SiCl to give Me$_3$SiCHI$_2$ (**1**). A one-pot transformation of aldehydes to (*E*)-1-alkenyltrimethylsilanes is then performed with iodoform, manganese, Me$_3$SiCl, and a catalytic amount of chromium(II) chloride in THF via in situ formation of **1**.

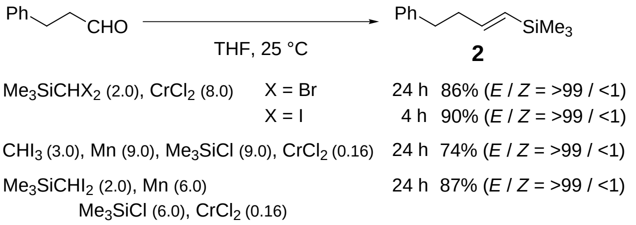
Keywords: geminal dichromium reagent, geminal diiodo compound, (*E*)-1-alkenylsilane, chromium(II), chromium(III), manganese

Manganese metal has a reducing ability between that of samarium(II) and zinc, and is employed in organic synthesis after appropriate activation.[1] One of the typical methods for activating metals such as manganese is by treatment with Me$_3$SiCl.[2] When active halogen compounds were treated with manganese and Me$_3$SiCl, reduction of the halogen and successive silylation was found to occur. For example, treatment of iodoform with manganese in THF in the presence of an excess amount of Me$_3$SiCl afforded Me$_3$SiCHI$_2$ (**1**) in 33% yield (eq 1).[3] In this reaction, a trimethylsilyl group selectively replaced one of the three iodine atoms. The yield of **1** improved to 59%, when DME was used as a solvent and NaI was added.



Equation 1

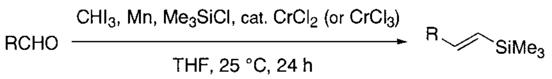
The selective iodine-silicon exchange of iodoform prompted us to improve a chromium-based transformation of aldehydes into (*E*)-alkenylsilanes reported previously.[4,5] In this transformation, a geminal dichromium reagent was prepared by reduction of Me$_3$SiCHBr$_2$ with chromium(II) chloride, and the reagent added to aldehydes without affecting the coexisting ketone and ester groups due to the mild nucleophilicity of the organochromium reagent.[6] However, there are two disadvantages: First, Me$_3$SiCHBr$_2$ should be prepared in advance by deprotonation and silylation from dibromomethane, which requires using a strong base under a carefully controlled low temperature.[7] Second, chromium(II) chloride is a one-electron reductant, thus, 8 equiv. of the salt is usually necessary to obtain reasonable yields. Recently, Fürstner succeeded in reducing the amount of chromium(II) by using manganese metal and Me$_3$SiCl in the reaction of allyl- and alkenylchromium reagents.[8] Therefore, the two disadvantages can be overcome using the manganese metal.



Equation 2

A THF solution of iodoform was added to a mixture of manganese, Me$_3$SiCl, and a catalytic amount of CrCl$_2$ in THF. The mixture was stirred at 25 °C for 5 min, and 3-phenylpropanal was added to the mixture. The resulting mixture was stirred at 25 °C for 24 h. After usual workup and purification, (*E*)-alkenylsilane **2** was produced stereoselectively in 74% yield along with 4-phenyl-1-butene (**3**) in 11% yield (eq. 2); 4-Phenyl-1-iodo-1-butene (**4**), which is produced by a reaction of iodoform and chromium(II) chloride,[9] was not detected.[10] The transformations from some aldehydes are summarized in Table 1. (*E*)-Isomers of alkenylsilanes were selectively produced in all cases. A ketone group was untouched during the transformation (run 4).

Table 1 Transformation of Aldehydes to (*E*)-Alkenylsilanes.[a]

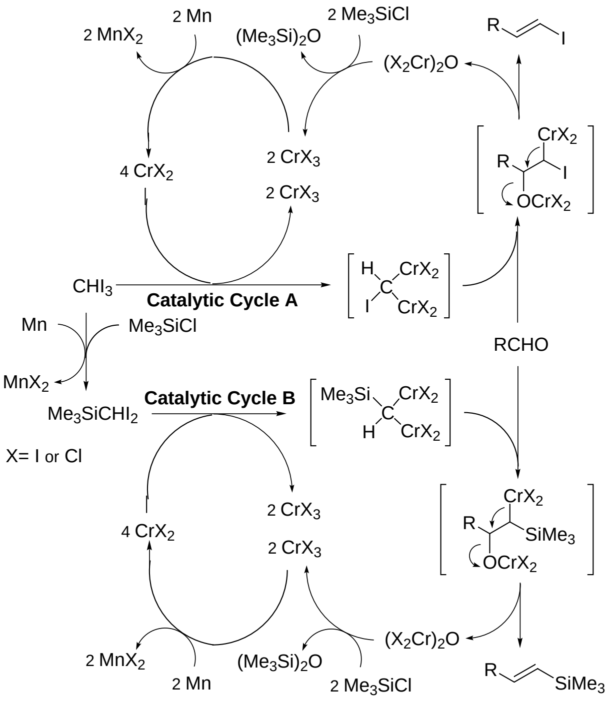


run	aldehyde	CrCl$_2$		CrCl$_3$	
		silane Y / %	alkene Y / %	silane Y / %	alkene Y / %
1	*n*-C$_8$H$_{17}$CHO	74	11	60	7
2	c-C$_6$H$_{11}$CHO	76[b]	9[b]	61[b]	13[b]
3	PhCHO	80	12	58	13
4	MeCO(CH$_2$)$_8$CHO	73	5	61	7

[a] Reactions were conducted on a 2.0 mmol scale. Iodoform (3.0 mol), Mn (9.0 mol), Me$_3$SiCl (9.0 mol), and CrCl$_2$ (or CrCl$_3$) (0.16 mol) were used per mol of aldehyde. Isolated yields. [b] GLPC yields.

Under standard reaction conditions (Table 1, run 1), compounds were recovered in the following order: 1-dodecene (98%); 1-dodecyne (99%); 1-chlorododecane (99%); ethyl octanoate (94%); nonanenitrile (92%). In contrast to a stoichiometric reaction with $CrCl_2$ in which nonanal ethylene acetal was recovered in 97% yield, the compound was recovered in only 24% yield during the transformation. This was probably due to the formation of Me_3SiI.

A plausible mechanism for the $CrCl_2$-manganese-promoted formation of alkenylsilane is shown in Scheme 1.[11] Iodoform is reduced with 1 equiv. of manganese in THF to form $IMnCHI_2$, which is trapped with Me_3SiCl to give Me_3SiCHI_2. Reduction of Me_3SiCHI_2 with 4 equiv. of chromium(II) gives the corresponding geminal dichromium reagent, which reacts with an aldehyde followed by elimination of $X_2Cr{-}O{-}CrX_2$ to afford an alkenylsilane. The formed $X_2Cr{-}O{-}CrX_2$ is converted to chromium(III) halide with Me_3SiCl, and the chromium(III) is then reduced with manganese to reproduce chromium(II).[12] Thus, 3 equiv. of both manganese and Me_3SiCl are necessary for this transformation.



Scheme 1

Two important factors for the preferential formation of an alkenylsilane over an iodoalkene are shown to be 1) a catalytic amount of $CrCl_2$, and 2) a mixture of iodoform, Me_3SiCl, manganese, and $CrCl_2$, which is stirred for 5 min before addition of an aldehyde. For example, when the amount of $CrCl_2$ was increased to stoichiometric (9.0 equiv.) in the typical procedure (eq. 2, line 3), the product distribution changed markedly; Iodoalkene **4** was obtained in 74% yield (E / Z = 81 / 19) as a major product and alkenylsilane **2** was produced in only 9% yield.[13] Addition of iodoform and 3-phenylpropanal at the same time in this catalytic $CrCl_2$ system also increased the amount of iodoalkene **4**. Iodoalkene **4**, alkenylsilane **2**, and alkene **3** were produced in 52%, 21%, and 9% yields, respectively. Because the catalytic cycle **A** proceeds quickly,[14] simultaneous addition of iodoform and an aldehyde produced a similar effect as increasing the amount of $CrCl_2$. Formation of iodoalkene **4** was suppressed by pre-stirring the mixture of iodoform, Me_3SiCl, manganese, and a catalytic amount of $CrCl_2$ at 25 °C for 5 min before addition of 3-phenylpropanal, probably due to the consumption of iodoform leading to Me_3SiCHI_2.

Typical Procedure

Under an argon atmosphere, Me_3SiCl (2.3 mL, 18 mmol) was added at 25 °C to a suspension of $CrCl_2$ (39 mg, 0.32 mmol),[15] and manganese (0.99 g, 18 mmol)[16] in THF (12 mL). After stirring the mixture at 25 °C for 30 min, a solution of iodoform (2.4 g, 6.0 mmol) in THF (8 mL) was added to the mixture at 25 °C over a period of 5 min, and the mixture was stirred for 5 min. A solution of 3-phenylpropanal (0.27 g, 2.0 mmol) in THF (8 mL) was added to the mixture at 25 °C over a period of 5 min and the resulting mixture was stirred at 25 °C for 24 h. The color of the mixture gradually turned from dark red to brown while stirring. The reaction mixture was poured into water (50 mL) and the mixture was extracted with hexane (3x40 mL). The organic extracts were washed with aqueous $Na_2S_2O_3$ and brine, dried over anhydrous $MgSO_4$ and concentrated. Purification by column chromatography on silica gel (hexane) gave trimethyl((*E*)-4-phenyl-1-butenyl)silane (**2**) in 74% yield (0.30 g, E / Z = >99 / <1) as a colorless oil along with 4-phenyl-1-butene (**3**, 29 mg, 11%).

Acknowledgement

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(10) 4-Phenyl-1-iodo-1-butene (**4**) was reduced to 4-phenyl-1-butene (**3**) under the reaction conditions (25 °C, 24 h).

(11) Stirring a mixture of iodoalkene **4**, iodoform, manganese, and Me_3SiCl, and a catalytic amount of chromium(II) chloride at 25 °C for 24 h did not afford alkenylsilane **2**; iodoalkene **4** was recovered in 66% yield along with alkene **3** in 20% yield. The result suggests that alkenylsilane **2** was not produced via reductive iodine-silicone exchange of iodoalkene **4**.

(12) A catalytic amount of $CrCl_3$ can be used for the transformation, however the yields are somewhat lower than those with $CrCl_2$ (Table 1). Chromium(III) hexahydrate (99.995% purity) was purchased from Aldrich Chemical Co. and dehydrated by treatment with thionyl chloride. Pray, A. R. *Inorg. Synth.* **1954**, *5*, 153.

(13) The reaction was finished within 1 h at 25 °C.

(14) The chromium(II)-reduction of Me_3SiCHI_2 to the corresponding geminal dichromium reagent (Catalytic Cycle **B**) proved to proceed slower than that of iodoform (Catalytic Cycle **A**). For example, addition of 3-phenylpropanal to a mixture of iodoform (0.1 equiv.), Me_3SiCHI_2 (0.1 equiv.), and $CrCl_2$ (0.4 equiv.) at 25 °C, followed by stirring for 3 h produced iodoalkene **4** in 73% yield (based on $CrCl_2$); Alkenylsilane **2** was not detected. Recovery of iodoform and Me_3SiCHI_2 were in 7% and 79% yields, respectively.

(15) Chromium(II) chloride (99.9% purity) was purchased from Aldrich Chemical Co.

(16) Manganese powder was purchased from Kojundo Chemical Laboratory Co. (99.9% purity, -50 mesh). The powder was used for reactions without purification.

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