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Manganese-Catalyzed Reaction of *gem*-Dibromoalkanes with Grignard Reagents. Selective Synthesis of Alkenylsilanes

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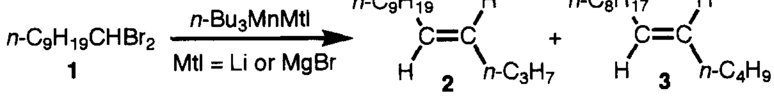
Abstract: Treatment of dibromomethyltrialkylsilanes with butylmagnesium bromide in the presence of a catalytic amount of manganese(II) chloride provided (*E*)-1-trialkylsilyl-1-pentenes with high stereoselectivity in good yields. © 1997 Elsevier Science Ltd.

Recently, we have reported that the reaction of *gem*-dibromocyclopropanes with trialkylmanganate followed by treatment with electrophiles provides dialkylated cyclopropanes.[1] Here we describe that the treatment of *gem*-dibromoalkanes with trialkylmanganate,[2,3] derived from manganese(II) chloride and three equivalents of Grignard reagent or alkyllithium, affords alkenes and also that the reaction of *gem*-dibromoalkanes with alkylmagnesium halides takes place in the presence of a catalytic amount of manganese(II) chloride.

Manganese(II) chloride (189 mg, 1.5 mmol) was sonicated in tetrahydrofuran (THF, 10 ml) under argon atmosphere for 10 min. Butyllithium (1.5 *M* hexane solution, 3.0 ml, 4.5 mmol) was added to the suspension of $MnCl_2$ in THF at 0 °C. The mixture turned into a clear brown solution and, after being stirred for 20 min at 0 °C, a solution of 1,1-dibromodecane (**1**, 0.30 g, 1.0 mmol) in THF (2 ml) was added at 0 °C and the whole was stirred at 0 °C for 1 h and then at 25 °C for another 1 h. Extractive workup followed by silica-gel column chromatography gave a mixture of 4-tetradecene (**2**, *E*/*Z* = 92/8) and 5-tetradecene (**3**, *E*/*Z* = 92/8) in 95% combined yield (0.19 g, **2**/**3** = 1/1) (Scheme 1). The use of butylmagnesium bromide in place of butyllithium gave the same isomeric mixtures **2** and **3** (**2**/**3** = 1/1) in 91% yield. The reaction proved to proceed in the presence of a catalytic amount of manganese(II) chloride. Thus, an addition of a solution of **1** (1.0 mmol) to a THF solution of butylmagnesium bromide (3.0 mmol) and manganese chloride (12 mg, 10 mol%) at 0 °C provided **2** and **3** in 83% combined yield.

Scheme 1



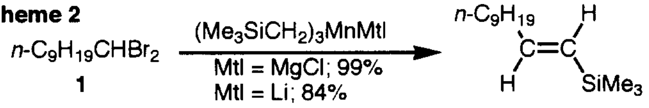
The reaction was applied to the preparation of alkenylsilanes[4] and the representative results are shown in Table 1 and Scheme 2. Several comments are worth noting. (1) Stoichiometric reaction and catalytic reaction were equally effective for the formation of 1-trialkylsilyl-1-alkenes. (2) (*E*)-Alkenylsilanes were obtained exclusively and no trace of the *Z*-isomer could be detected in the reaction mixture. (3) Among various manganese salts examined, MnCl_2, Mn(acac)_3, and $\text{Mn}_2\text{(CO)}_{10}$ proved to be good catalysts. For instance, treatment of *i*-$\text{Pr}_3\text{SiCHBr}_2$ with ethylmagnesium bromide in the presence of these catalysts gave (*E*)-1-triisopropylsilyl-1-propene in 88%, 74%, or 85% yield, respectively. (4) Diiodide (*t*-$\text{BuMe}_2\text{SiCHI}_2$) was as reactive as dibromide **4b** and afforded the 1-*tert*-butyldimethylsilyl-1-pentene in 88% yield upon treatment with *n*-Bu_3MnLi. Dichloride (*t*-$\text{BuMe}_2\text{SiCHCl}_2$) was less reactive than **4b**, and the reaction with *n*-Bu_3MnLi gave the same alkenylsilane in 57% yield after prolonged reaction time (25 °C, 21 h). (5) The reaction of 1,1-dibromodecane **1** with tris(trimethylsilylmethyl)manganate gave 1-trimethylsilyl-1-undecene exclusively and no isomeric allylic silane (1-trimethylsilyl-2-undecene) could be detected (Scheme 2). The hydrogen on the carbon-bearing trimethylsilyl group was eliminated selectively.

Table 1. Preparation of (*E*)-1-Trialkylsilyl-1-alkene[a]

Entry		Substrate	Reagent	Yield (%)
1	**4a**	$\text{Ph}_2\text{MeSiCHBr}_2$[b]	Me_3MnMgI	89
2	**4a**	$\text{Ph}_2\text{MeSiCHBr}_2$[b]	Et_3MnMgBr	76
3	**4a**	$\text{Ph}_2\text{MeSiCHBr}_2$[b]	*n*-Bu_3MnLi	95
4	**4a**	$\text{Ph}_2\text{MeSiCHBr}_2$[b]	$(\text{PhCH}_2)_3\text{MnMgBr}$	88
5	**4b**	*t*-$\text{BuMe}_2\text{SiCHBr}_2$	$(\text{Me}_3\text{SiCH}_2)_3\text{MnMgCl}$	57
6	**4b**	*t*-$\text{BuMe}_2\text{SiCHBr}_2$	*n*-Bu_3MnMgBr	72
7	**4b**	*t*-$\text{BuMe}_2\text{SiCHBr}_2$	*n*-Bu_3MnLi	96
8	**4c**	*i*-$\text{Pr}_3\text{SiCHBr}_2$	Et_3MnMgBr	79
9	**4a**	$\text{Ph}_2\text{MeSiCHBr}_2$[b]	*n*-$\text{C}_4\text{H}_9\text{MgBr/MnCl}_2$	67
10	**4a**	$\text{Ph}_2\text{MeSiCHBr}_2$[b]	*n*-$\text{C}_{16}\text{H}_{33}\text{MgBr/MnCl}_2$	62
11	**4b**	*t*-$\text{BuMe}_2\text{SiCHBr}_2$	*n*-$\text{C}_4\text{H}_9\text{MgBr/MnCl}_2$	87
12	**4c**	*i*-$\text{Pr}_3\text{SiCHBr}_2$	EtMgBr/MnCl_2	88
13	**4c**	*i*-$\text{Pr}_3\text{SiCHBr}_2$	MeMgI/MnCl_2	75
14	**4d**	$\text{Me}_3\text{SiCHBr}_2$	*n*-$\text{C}_8\text{H}_{17}\text{MgBr/MnCl}_2$	76
15	**4e**	(*c*-$\text{C}_6\text{H}_{11})_2\text{MeSiCHBr}_2$[c]	*n*-$\text{C}_4\text{H}_9\text{MgBr/MnCl}_2$	95

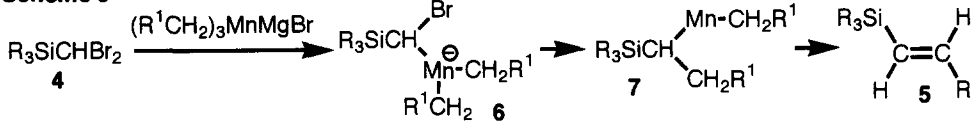
a) Stoichiometric reactions were performed with $\text{R}_3\text{SiCHBr}_2$ (1.0 mmol) and manganate (1.2 mmol) at 0 °C unless otherwise noted. In the catalytic reactions, Grignard reagent (3.0 mmol), $\text{R}_3\text{SiCHBr}_2$ (1.0 mmol) and MnCl_2 (5 mol%) were employed. b) The reactions were performed at 25 °C. c) *c*-C_6H_{11} = cyclohexyl.

Scheme 2



We are tempted to assume the following reaction mechanism for the stoichiometric reaction:[5] (1) initial halogen-manganese exchange to give **6**, (2) alkyl migration under Br^- elimination providing **7**, (3) elimination of Mn and hydrogen at the β-position[6] (Scheme 3).

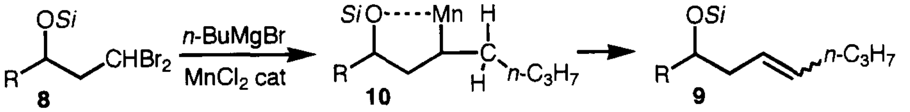
Scheme 3



The facility of Mn-H elimination depended on the nature of substituents on silicon. In the case of trialkylsilyldibromomethane such as **4b**, **4c**, **4d**, and **4e**, elimination took place easily at 0 °C for 2 h. On the other hand, the elimination from $Ph_2MeSiCH(MnEt)Et$, derived from the reaction of **4a** with triethylmanganate, was slow and diphenylmethylpropylsilane was obtained in 17% yield along with alkenylsilane (47%). Thus, the reaction temperature was raised and the reaction mixture of **4a** was stirred at 25 °C for 2 h to suppress the formation of diphenylmethylpropylsilane (<5%).

In the reaction of 1,1-dibromodecane with butylmagnesium, two regioisomeric alkenes were produced as shown in Scheme 1 because of the presence of two types of β-hydrogens. The reaction is not useful for synthetic purposes. However, treatment of dibromoalkane **8**, generated from epoxide and *tert*-butyldimethylsilyldibromomethyllithium,[7] with butylmagnesium bromide in the presence of $MnCl_2$ catalyst gave alkene **9** as a single regioisomer. The coordination of oxygen of the siloxy group to manganese would cause formation of five-membered ring intermediate **10** in which only one hydrogen is available for *syn*-elimination of Mn-H (Scheme 4).[8]

Scheme 4



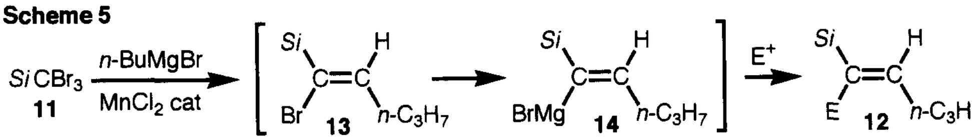
Si = *t*-BuMe$_2$Si

R = CH_3 60% *E*/*Z* = 92/8

R = Ph 68% *E*/*Z* = 91/9

Tribromomethyltrialkylsilane, *t*-BuMe$_2$SiCBr$_3$ (**11**) afforded alkenylsilane **12** upon treatment with *n*-BuMgBr under $MnCl_2$ catalysis. Addition of an electrophile such as D_2O, allyl bromide, or benzaldehyde provided the corresponding adducts in good yields. The results supported that an intermediary bromoalkene **13** was converted into alkenylmagnesium species **14** through metal-halogen exchange under the reaction conditions (Scheme 5).

Scheme 5



Si = *t*-BuMe$_2$Si

12a : E = H, 53% (*E*/*Z* = 89/11) **12b** : E = D, 54%

12c : E = CH_2 = CH–CH_2, 68% **12d** : E = PhCH(OH), 58%

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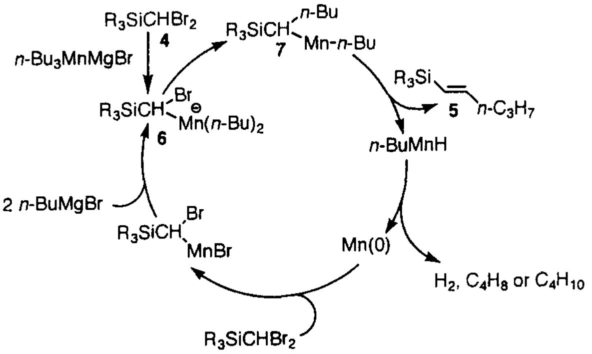
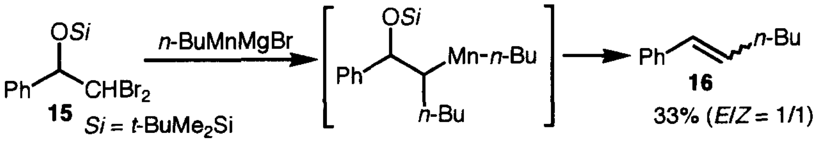
5. The reaction mechanism for catalytic pathway could be as follows. Low-valent manganese species Mn(0), generated from *n*-BuMnH, would insert into one of the carbon-bromine bonds to give $R_3SiCH(Br)MnBr$. An attack of two equivalents of *n*-BuMgBr on $R_3SiCH(Br)MnBr_2$ regenerates **6**. Oxidative insertion of manganese into organic halides has been reported. Hiyama, T.; Obayashi, M.; Nakamura, A. *Organometallics* **1982**, *1*, 1249–1251; Kim, S.-H.; Hansen, M. V.; Rieke, R. D. *Tetrahedron Lett.* **1996**, *37*, 2197–2200; Fürstner, A.; Brunner, H. *Tetrahedron Lett.* **1996**, *37*, 7009–7012; Takai, K.; Ueda, T.; Hayashi, T.; Moriwake, T. *Tetrahedron Lett.* **1996**, *37*. 7049–7052.



6. Decomposition of the dialkylmanganese species has been reported to proceed by α,β-elimination of an hydrido-manganese species. Tamura, H.; Kochi, J. *J. Organomet. Chem.* **1971**, *29*, 111–129. They mentioned that secondary alkyl manganese has decomposed much more easily than primary one.
7. Shinokubo, H.; Miura, K.; Oshima, K.; Utimoto, K. *Tetrahedron,* **1996**, *52*, 503–513.
8. β-Siloxydibromo compound such as **15**, derived from the reaction of benzaldehyde with *tert*-butyldimethylsilyldibromomethyllithium,[7] gave alkene **16** via the elimination of $Mn\text{-}OSiMe_2\text{-}t\text{-}Bu$ instead of elimination of the Mn-H unit.



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