Reaction of 1,3-Dihalopropene with Trialkylmanganate

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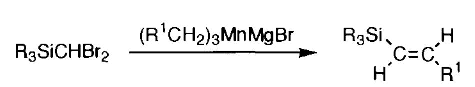
(Received September 12, 1997; CL-970708)

A three-component coupling reaction was performed. Treatment of 1,3-dibromopropene or 1,3-dichloropropene with tributylmanganate (n-Bu$_3$MnLi) provided a butylated allylmanganese compound which could be trapped by an electrophile such as benzaldehyde.

Recently, we have reported the dialkylation reaction of *gem*-dibromocyclopropanes upon treatment with trialkylmanganate followed by an addition of electrophiles.[1] Application of this reaction to the preparation of alkenylsilanes has also been reported (eq. 1).[2] Here we wish to report that the treatment of 1,3-dibromopropene or 1,3-dichloropropene with trialkylmanganate followed by addition of an electrophile such as aldehyde provides a homoallylic alcohol.[3]

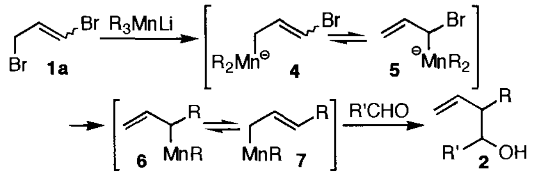

(1)

$$R_3SiCHBr_2 \xrightarrow{(R^1CH_2)_3MnMgBr} \begin{matrix} R_3Si & & H \\ & C=C & \\ H & & R^1 \end{matrix} \qquad (1)$$

A solution of 1,3-dibromopropene **1a**[4] (0.20g, 1.0 mmol) in THF (3 ml) was added to a solution of tributylmanganate (1.5 mmol), generated from MnCl$_2$ (1.5 mmol) and n-BuLi (4.5 mmol), in THF (10 ml) at 0 °C under argon atmosphere. The mixture was stirred at 0 °C for 1 h, then benzaldehyde (3.0 mmol) was added. The whole was stirred for another 30 min at 0 °C and the resulting mixture was poured into water. Extractive workup (AcOEt/brine) followed by silica-gel column purification provided homoallylic alcohol **2a** (151 mg) in 74% yield.

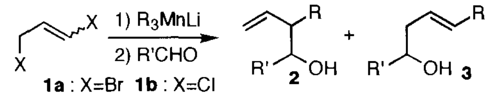
The representative results are shown in Table 1. The use of n-BuMgBr in place of n-BuLi also provided the desired homoallylic alcohols. The regioisomeric products **3** were obtained in the case of the reaction of benzaldehyde with trialkylmanganate derived from a Grignard reagent (Entries 5, 8 and 9).[5] Treatment of 1,3-dibromopropene with trimethylmanganate (Me$_3$MnLi) gave no three-component coupling product and 1-phenylethanol was obtained as the main product.

We are tempted to assume the following reaction mechanism for the reaction (eq. 2): (1) allylic halogen-manganate exchange to give **4**[6,7], (2) isomerization of allylmanganate **4** into **5**, (3) 1,2-alkyl group migration from manganese to an adjacent carbon under elimination of Br$^-$ providing **6**, then (4) addition of an electrophile to the resulting allylic manganate **6** and/or **7** to afford homoallylic alcohol **2**.[8]



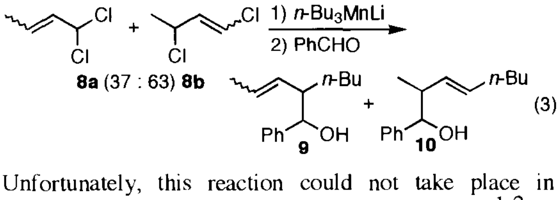
(2)

Table 1. Reaction of 1,3-Dihalopropene with Trialkylmanganate



Entry	X	R$_3$MnLi	R'CHO	Product/%	
				2 (*threo*:*erythro*)	**3**
1	Cl	n-Bu$_3$MnLi	PhCHO	56 (70:30)	0
2	Cl	n-Bu$_3$MnLi	c-C$_6$H$_{11}$CHO	49 (68:32)	0
3	Br	n-Bu$_3$MnLi	PhCHO	74 (68:32)	0
4	Br	n-Bu$_3$MnLi	c-C$_6$H$_{11}$CHO	69 (89:11)	0
5	Br	n-Bu$_3$MnMgBr	PhCHO	71 (75:25)	15
6	Br	n-Bu$_3$MnMgBr	i-PrCHO	70 (92:8)	0
7	Br	n-Bu$_3$MnMgBr	t-BuCHO	67 (95:5)	0
8	Br	Et$_3$MnMgBr	PhCHO	64 (71:29)	11
9	Br	n-Oct$_3$MnMgBr	PhCHO	72 (74:26)	19
10	Br	n-Oct$_3$MnMgBr	i-PrCHO	70 (92:8)	0

Addition of an isomeric mixture of 1,1-dichloro-2-butene (**8a**) and 1,3-dichloro-1-butene (**8b**) to tributylmanganate followed by treatment with benzaldehyde afforded an isomeric mixture of homoallylic alcohols **9** and **10** in 44% combined yield (**9**:**10** = 1:1) (eq. 3).[9]



(3)

Unfortunately, this reaction could not take place in the presence of a catalytic amount of manganese chloride.[1,2] Thus, treatment of **1a** with n-BuMgBr in the presence of a catalytic amount of MnCl$_2$ (10 mol%) followed by an addition of benzaldehyde provided no homoallylic alcohol.[10]

References and Notes

1 R. Inoue, H. Shinokubo, and K. Oshima, *Tetrahedron Lett.*, **37**, 5377 (1996).

2 H. Kakiya, R. Inoue, H. Shinokubo, and K. Oshima, *Tetrahedron Lett.*, **38**, 3275 (1997).

3 Preparation of organozinc species by similar alkyl migration using trialkylzincate was reported. T. Harada, T. Katsuhira, A. Osada, K. Iwazaki, K. Maejima, A. Oku, *J. Am. Chem. Soc.*, **118**, 11377 (1996).

4 1,3-Dibromopropene and 1,3-dichloropropene were purchased from Aldrich Chemical Company, Inc. and Tokyo Kasei Co. Ltd., respectively, and used without further purification. A mixture of 1,3-dichloro-1-butene and 1,1-

dichloro-2-butene was prepared according to the reported procedure: L. J. Andrews, *J. Am. Chem. Soc.*, **68**, 2584 (1946).

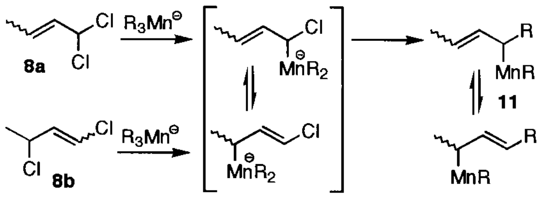
5 Although the origin of the different selectivities between the reaction with *n*-BuLi and that with *n*-BuMgBr (Entry 3 and 5 in Table 1) is not clear at this stage, it might be attributed to some effect of the existing metal salt (LiBr or $MgBr_2$) in the mixture.

6 In fact, treatment of allyl bromide with tributylmanganate (*n*-Bu_3MnLi) gave allylmanganate, as judged from formation of homoallylic alcohol ($PhCH(OH)CH_2CH=CH_2$, 60%) by an addition of benzaldehyde.

7 Preparative methods for allylmanganate have been reported: K. Takai, T. Ueda, T. Hayashi, and T. Moriwake, *Tetrahedron Lett.*, **37**, 7049 (1996); T. Hiyama, M. Obayashi, and A. Nakamura, *Organometallics*, **1**, 1249 (1982); T. Hiyama, M. Sawahata, M. Obayashi, *Chem. Lett.*, **1983**, 1237; G. Cahiez and P.-Y. Chavant, *Tetrahedron Lett.*, **30**, 7373 (1989).

8 A referee suggested an alternative reaction scheme; (1) S_N2' displacement of bromide with butyl group from *n*-Bu_3MnLi to give *n*-$BuCHBrCH=CH_2$ and (2) bromine-manganese exchange between the resulting allylic bromide and *n*-Bu_2Mn. We can not deny this possibility and need further study to decide the reaction mechanism.

9 It is difficult to obtain **8a** or **8b** in pure form. However, a mixture of **8a** and **8b** could be used because the same intermediary allylmanganese compound **11** were formed upon treatment with R_3MnMtl.



(4)

10 Treatment of **1a** with octylmagnesium bromide without $MnCl_2$ gave a complex mixture which mainly contains 1-bromo-1-undecene and 3-bromo-1-undecene.