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Generation of Allylic Manganates from Trimethylmanganate and Allylic Stannanes and Their Reactions with Epoxides

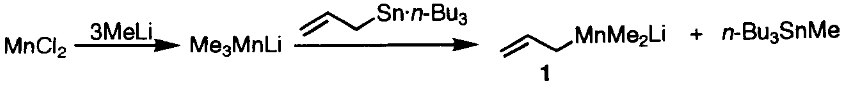
Jun Tang, Hideki Yorimitsu, Hirotada Kakiya, Rie Inoue, Hiroshi Shinokubo, and Koichiro Oshima*

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-01, Japan

Abstract: A new method for forming allyldimethylmanganate has been developed. The preparation eliminated the need for prior generation of an allylmetal species such as allyllithium or allylmagnesium compounds. The reagents reacted with epoxides to give allylated products exclusively in good yields.

The reactions of allylic organometallic compounds such as allylmagnesium, allylzinc, and allylcuprate with electrophiles have been widely studied.[1] In contrast, only few organomanganese reactions involving allylic manganese have been reported. Hiyama *et al.* reported that treatment of "Mn(0)" reagent, prepared in situ from anhydrous $MnCl_2$ and $LiAlH_4$ in THF, with allylic bromide and then with aldehydes provided homoallylic alcohols.[2] Metallic manganese powder suspended in THF containing iodine or $PbCl_2/Me_3SiCl$ has been also applied to Barbier-type allylation of carbonyl compounds.[3] An allylmanganese reagent, (allyl)MnCl, derived from allylmagnesium halide and $MnCl_2$, has been reported to react with α,β-unsaturated carbonyl compounds.[4] Recently, we have reported that triallylmanganate, ($(allyl)_3MnMgX$), generated from $MnCl_2$ and three equivalents of allylmagnesium halide, proved to be highly reactive toward various electrophiles.[5] We now report an alternative route to the allylic manganate species based on transmetallations of precursor allylstannanes.[6]

Treatment of allyltributylstannane (1.0 mmol) with Me_3MnLi (1.0 mmol), generated from $MnCl_2$ (1.0 mmol) and MeLi (3.0 mmol), in THF at 0 °C for 20 min afforded allyldimethylmanganate **1** essentially quantitatively, as judged from quantitative formation of $MeSn\text{-}n\text{-}Bu_3$. Similar conditions can be employed for the reaction of Me_3MnLi with other allylic stannanes such as methallyl-, crotyl-, and prenyltributylstannanes.[7]



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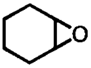
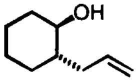
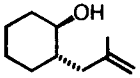
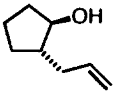
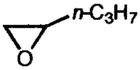
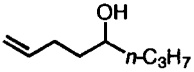
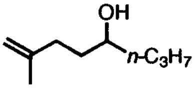
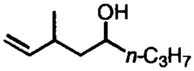
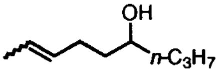
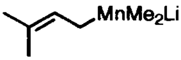
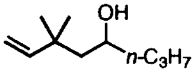
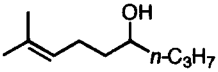
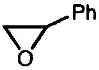
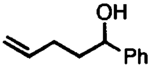
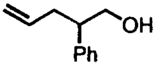
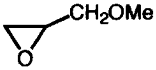
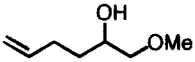
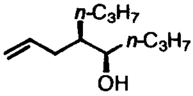
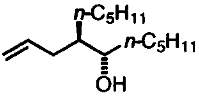
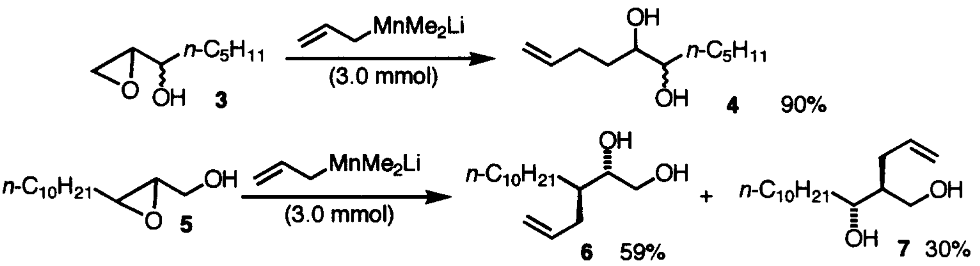
The reaction of allylic manganates with epoxides has been investigated. Table 1 shows representative results.[8] Several comments are worth noting. (1) Treatment of Me_3MnLi with 2 equivalents of allyltributylstannane provided the corresponding diallylmethylmanganate **2**[9] which reacted with epoxide (propyloxirane) equally as well as allyldimethylmanganate **1** to give the allylated products in 80% yield (based on propyloxirane employed). We chose allyldimethylmanganate **1** from the economical point of view since a

Table 1. Reaction of Allyldimethylmanganate with Epoxides

Entry	Substrate	Reagent	Product	Yield (%)
1				80
2				88
3				67
4				81
5				75
6			 	54 18
7			 	52 13
8			 	64 32
9				75
10				61
11				65

second allyl moiety could not be utilized effectively in the case of diallylmethylmanganate **2**. (2) Trimethylmanganate (Me_3MnLi) itself was much less reactive than allyldimethylmanganate toward epoxides. For instance, treatment of *cis*-2,3-dipentyloxirane with Me_3MnLi at 0 °C for 30 min and then at 25 °C for 1 h resulted in recovery of the oxirane (90%). (3) Tributylmanganate (n-Bu_3MnLi) was inferior to trimethylmanganate for the transmetallation with allylstannanes. Thus, the reaction of propyloxirane with allyldibutylmanganate ((allyl)Mn-n-Bu_2Li), derived from n-Bu_3MnLi and allyltributylstannane, afforded 7-octen-4-ol in only 40% yield under the same reaction conditions as the reaction with allyldimethylmanganate **1** (Entry 4).[10] (4) A counter metal cation of the ate complex played a critical role in the transmetallation. The transmetallation did not proceed between allylstannanes and trimethylmanganate ($Me_3MnMgBr$) derived from $MnCl_2$ and 3 equivalents of methylmagnesium bromide. (5) Crotylmanganate and prenylmanganate reacted preferentially with epoxides at the γ-carbon. However, the selectivities were inferior to those with allylcuprates (Entries 6 and 7).[6] (6) Cyclic epoxides, highly prone toward Lewis acid-induced rearrangement to cyclic ketones,[11] underwent clean displacement without formation of Lewis acid related side-products (Entries 1–3). (7) Whereas allylic manganate attacked the less hindered carbon of mono-substituted epoxides (Entries 4, 5, 6, 7, and 9), the attack of the allylic moiety on the carbon bearing a phenyl group competed with the attack on the less hindered carbon in the case of phenyloxirane (Entry 8). (8) The reaction proceeded stereospecifically. *Trans* epoxide (Entry 10) provided an *syn* product exclusively and *cis* epoxide (Entry 11) afforded *anti*-isomer as a single product. (9) Only the allylic moiety reacted with epoxides and no methylated product was observed in the reaction mixture.[12]

Treatment of α,β-epoxy alcohols **3**, **5** with allyldimethylmanganate **1** afforded diols. The reaction of **3** with **1** afforded 1,2-diol **4** selectively. Meantime, the epoxy alcohol **5** provided a mixture of 1,2-diol **6** and 1,3-diol **7**.



Next, the reaction of **1** with alkyl halides was studied. The manganate **1** proved to react with not only allylic halides but also ordinary alkyl halides. For instance, treatment of cinnamyl chloride (**8a**) or 1-bromo-2-tridecene (**8b**) with **1** provided 1-phenyl-1,5-hexadiene (**9a**, 78%) or an isomeric mixture of 1,5-hexadecadiene (**9b**) and 3-decyl-1,5-hexadiene (**10b**) (**9b**:**10b** = 9:1, 90% combined yield). The reaction of **1** with iodooctane or 3-phenylpropyl bromide gave 1-undecene or 6-phenyl-1-hexene in 80% or 82% yield, respectively.

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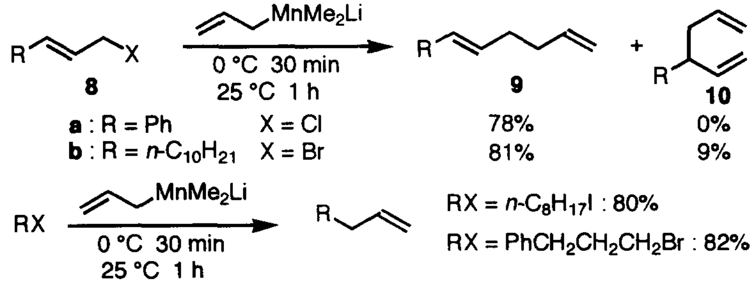

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7. The structure of crotylmanganate or prenylmanganate is not clear and might be contaminated by each regioisomer (CH_2=CHCHMeMnMe_2Li or CH_2=CHCMe_2MnMe_2Li).
8. Typical procedure for the reaction of allyldimethylmanganate **1** with epoxide is as follows. A THF suspension of manganese(II) chloride (0.19 g, 1.5 mmol) was sonicated for 20 min under argon atmosphere. The mixture was cooled to 0 °C, and methyllithium (1.0 M ether solution, 4.5 ml, 4.5 mmol) was added to give a clear brown solution. After the mixture was stirred for 20 min, a solution of allyltributylstannane (496 mg, 1.5 mmol) in THF (2 ml) was added, and the resulting dark-brown mixture was stirred for another 20 min. Then a solution of propyloxirane (86 mg, 1.0 mmol) in THF (1.5 ml) was added and the whole was stirred for 30 min at 0 °C and then for 1 h at 25 °C. The mixture was poured into 1N HCl (20 ml). Extraction with ethyl acetate (20 ml x 3) followed by silica gel column purification afforded 7-octen-4-ol (104 mg) in 81% yield.
9. Quantitative formation of MeSn-*n*-Bu_3 (2.0 mmol) was observed upon treatment of Me_3MnLi (1.0 mmol) with allyltributylstannane (2.0 mmol). Treatment of Me_3MnLi (1.0 mmol) with 3 equivalents of allyltributylstannane afforded a mixture of diallylmethylmanganate **2** and triallylmanganate which was judged from an isolation of 2.4 mmol of MeSn-*n*-Bu_3.
10. Treatment of allyltributylstannane (1.0 mmol) with *n*-Bu_3MnLi (1.0 mmol) in THF at 0 °C for 20 min provided tetrabutylstannane in only 40% yield.
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12. The reaction of allyldimethylmanganate **1** (1.5 mmol) with benzaldehyde (1.0 mmol) or cyclohexanecarbaldehyde (1.0 mmol) in THF at 0 °C for 1 h afforded a methylated product (22% or 19%) in addition to an allylated product (74 or 70%, respectively).

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