Allylmagnesation and Diallylation of Acetylenic Compounds Catalyzed by Manganese Salts

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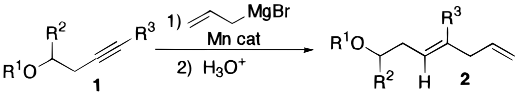
Allylic organometallic compounds have been studied extensively and widely used for highly stereoselective synthesis of homoallylic alcohols.[1] In contrast, only a few reports about the addition of allylic metals to triple bonds are found in the literature.[2] An allyl Grignard reagent adds to propargylic alcohols or homopropargylic alcohols by an *anti* addition process to give both regioisomers in the absence[3] or in the presence of CuI catalyst.[4] Allylzincation of terminal alkynes is generally complicated by competitive zincation of alkynes and double allylzincation.[5,6] Here we report that allylmagnesium bromide adds to the triple bond of the alkyl ether of homopropargylic alcohol to give monoallylated products with high regio- and stereoselectivities in the presence of a catalytic amount of manganese salt such as MnI$_2$, Mn(acac)$_3$, or Mn$_2$(CO)$_{10}$. The formation of diallylation products under an oxygen atmosphere is also disclosed.

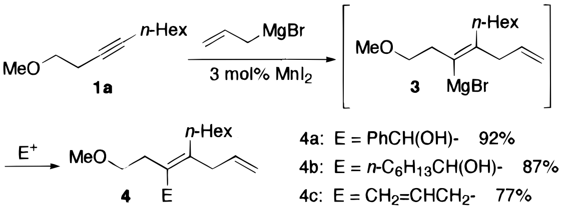
Treatment of an ethereal solution of homopropargylic alcohol methyl ether (**1a**, 1.0 mmol) with allylmagnesium bromide (1.5 mmol) in the presence of MnI$_2$ catalyst (3 mol %) at 25 °C for 3 h provided monoallylated product **2a** in 83% yield (eq 1).[7,8] Other manganese catalysts such as Mn(acac)$_3$, MeC$_5$H$_4$Mn(CO)$_3$, and Mn$_2$(CO)$_{10}$ were also effective for the reaction. The yields of **2a** with these catalysts were 93%, 89%, and 80%, respectively, under the same reaction conditions.[9] Benzyl ether of 3-decyn-1-ol (**1b**), THP ether of 3-decyn-1-ol (**1c**), methyl ether of 5-nonyn-3-ol (**1d**), or methyl ether of 4-phenyl-3-butyn-1-ol (**1e**) also gave the corresponding allylated product **2b**, **2c**, **2d**, or **2e** in 77%, 74%, 72%, or 74% yield, respectively, upon treatment with allylmagnesium bromide in the presence of Mn(acac)$_3$ (3 mol %) in toluene at 25 °C for 3 h. Other metallic catalysts such as PdCl$_2$(CH$_3$CN)$_2$, NiCl$_2$(PPh$_3$)$_2$, CrCl$_3$, and RuCl$_3$ were ineffective, and starting acetylenic compound **1a** was recovered unchanged.



(1)

a : R^1 = Me, R^2 = H, R^3= *n*-Hex b : R^1 = PhCH$_2$, R^2 = H, R^3 = *n*-Hex
c : R^1 = THP, R^2 = H, R^3 = *n*-Hex d : R^1 = Me, R^2 = Et, R^3 = *n*-C$_3$H$_7$
e : R^1 = Me, R^2 = H, R^3 = Ph

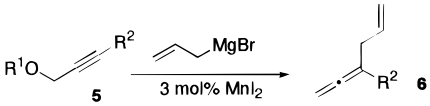
The intermediary alkenylmagnesium compound **3** could be trapped by electrophiles such as PhCHO, *n*-C$_6$H$_{13}$CHO, or allyl bromide (eq 2). The *syn* addition of an allyl−metal component was confirmed by comparison of **4c** with the authentic sample of *trans*-diallylated product derived from HOCH$_2$CH$_2$C≡C-*n*-Hex according to the reported procedure[3] (a, CH$_2$=CHCH$_2$MgBr, CuI; b, CH$_2$=CHCH$_2$Br; c, NaH, MeI).



4a: E = PhCH(OH)- 92%
4b: E = *n*-C$_6$H$_{13}$CH(OH)- 87%
4c: E = CH$_2$=CHCH$_2$- 77%

(2)

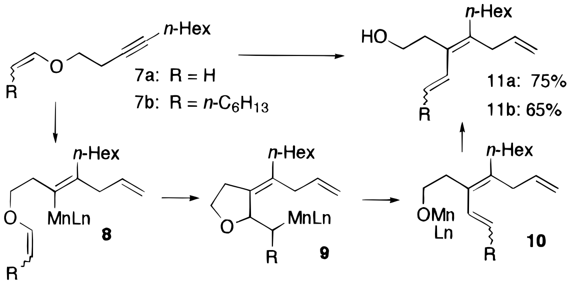
The reaction was clearly oxygen-assisted since the yield dropped to 42% in the case of the benzyl ether of 4-hexyn-1-ol, and 6-dodecyne was completely recovered even after heating a mixture at reflux in ether for 10 h. The use of propargylic alcohol alkyl ether **5** instead of the homopropargylic substrate afforded allenyl product **6** which was generated by S$_N$2′ type displacement of an alkoxy group by allylic anion (eq 3).[10]



(3)

a : R^1 = Me$_2$C=CHCH$_2$-, R^2 = *n*-C$_6$H$_{13}$: 56%
b : R^1 = Me, R^2 = *n*-C$_6$H$_{13}$: 56%

Next, the reaction of homopropargylic ether having an olefinic moiety has been examined. An addition of allylmagnesium bromide to a THF solution of homopropargyl alkenyl ethers **7a** and **7b** (*Z/E* = 90/10) in the presence of a catalytic amount of Mn(acac)$_3$ afforded tetrasubstituted alkene **11a** (75%) and **11b** (*Z/E* = 10/90, 65%)[11] with high stereoselectivity. We are tempted to assume following reaction mechanism: (1) allylmanganation of **7** gives alkenylmanganese intermediate **8**, (2) intramolecular carbomanganation provides furan derivative **9**, and (3) deoxymanganation followed by transmetalation and aqueous workup affords tetrasubstituted alkene **11** (eq 4).



(4)

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[1] Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207 and references cited therein. Recently conjugate addition of allylic copper species has been reported: Lipshutz, B. H.; Hackmann, C. *J. Org. Chem.* **1994**, *59*, 7437.

[2] Knochel, P. Carbometallation of Alkenes and Alkynes. In *Comprehensive Organic Synthesis*; Pergamon Press: Oxford, 1991; Vol. 4, p 865. Oppolzer, W. Metallo-ene Reactions. In *Comprehensive Organic Synthesis*; Pergamon Press: Oxford, 1991; Vol. 5, p 29.

[3] Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841. von Rein, F. W.; Richey, H. G., Jr. *Tetrahedron Lett.* **1971**, 3777.

[4] Jousseaume, B.; Duboudin, J.-G. *J. Organomet. Chem.* **1975**, *91*, C1.

[5] Bernadou, F.; Miginiac, L. *Tetrahedron Lett.* **1976**, 3083. Mauze, B.; Nivert, C.; Miginiac, L. *J. Organomet. Chem.* **1972**, *44*, 69. Bellassoued, M.; Frangin, Y. *Synthesis* **1978**, 838.

[6] Further examples about the addition of other allylic organometallic reagents to alkynes are as follows. Allylic aluminum reagents: Miller, J. A.; Negishi, E. *Tetrahedron Lett.* **1984**, *25*, 5863. Negishi, E.; Takahashi, T. *Synthesis* **1988**, 1. Allylic indium reagents: Araki, S.; Imai, A.; Shimizu, K.; Butsugan, Y. *Tetrahedron Lett.* **1992**, *33*, 2581. Allylic boron reagents: Mikhailov, B. M. *Pure Appl. Chem.* **1974**, *39*, 505. Mikhailov, B. *Organomet. Chem. Rev.* **1972**, *8* (A), 1.

[7] Allylic manganese reagent derived from allylic bromide and Mn(0) has been reported to react with aldehydes providing homoallylic alcohols. Hiyama, T.; Obayashi, M.; Nakamura, A. *Organometallics* **1982**, *1*, 1249.

[8] Three different types of organomanganous reagents (RMnX, R$_2$Mn, R$_3$Mn$^-$Mtl$^+$) have been reported. Normant, J. F.; Cahiez, G. Organomanganous reagents. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Otto Salle Verlag GmbH & Co.: Frankfurt am Main, 1983; Vol. 3.

[9] Toluene was used as a solvent instead of ether. In the case of MnI$_2$, ether was used because of its solubility.

[10] Burton, D. J.; Hartgraves, G. A.; Hsu, J. *Tetrahedron Lett.* **1990**, *31*, 3699. Westmijze, H.; Vermeer, P. *Ibid.* **1979**, 4101. Tadema, G.; Everhardus, R. H.; Westmijze, H.; Vermeer, P. *Ibid.* **1978**, 3935. Marek, I.; Mangeney, P.; Alexakis, A.; Normant, J. F. *Ibid.* **1986**, *27*, 5499.

[11] The formation of **11b** as a mixture of *Z/E* = 10/90 starting from **7b** (*Z/E* = 90/10) might suggest that both intramolecular carbomanganation and deoxymanganation proceed in *syn* fashion.

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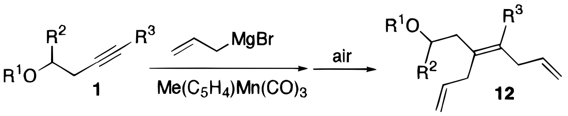
We have found accidentally that diallylation products[12] are formed along with the monoallylated one in the presence of oxygen. The nature of manganese catalysts and solvents has played a critical role for the successful formation of diallylation products. The manganese salt $MeC_5H_4Mn(CO)_3$ was a choice. Thus, treatment of a THF solution of **1a** (1.0 mmol) with allylmagnesium bromide (4.0 mmol) in the presence of $MeC_5H_4Mn(CO)_3$ (10 mol %) under an argon atmosphere for 2 h at 25 °C followed by exposure of the reaction mixture to air for 12 h gave the diallylated product **12a**=**4c** in 80% yield without contamination of the monoallylated product **2a** (eq 5).[13] Starting from **1b**, **1c**, and **1d**, the corresponding diallylated products **12b**, **12c**, and **12d** were obtained in 78%, 35%, and 78% yields, respectively, under the same reaction conditions. The use of $Mn(acac)_3$ instead of $MeC_5H_4Mn(CO)_3$ decreased the yield of the diallylated product **12a** to 66%, and the MnI_2-catalyzed reaction afforded a mixture of **2a** (42%) and **12a** (22%).[14]



(5)

Supporting Information Available: Text describing experimental details (6 pages). See any current masthead page for ordering and Internet access instructions.

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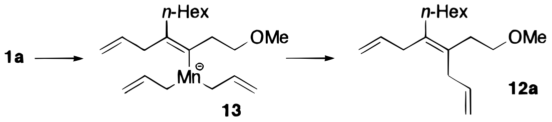
(12) Disilylation of acetylenes with a stoichiometric amount of $(R_3Si)_3MnMgMe$ has been reported. Hibino, J.; Nakatsukasa, S.; Fugami, K.; Matsubara, S.; Oshima, K.; Nozaki, H. *J. Am. Chem. Soc.* **1985**, *107*, 6416. Fugami, K.; Hibino, J.; Nakatsukasa, S.; Matsubara, S.; Oshima, K.; Utimoto, K.; Nozaki, H. *Tetrahedron* **1988**, *44*, 4277.

(13) We are tempted to assume that reductive elimination from alkenylmanganese intermediate **13** affords the diallylated product and low-valent manganese which is oxidized by air to manganese active species:



(14) Treatment of allyl propargyl ether **14** with allylmagnesium bromide under the same reaction conditions gave furan derivative **15** in only 27% yield in addition to allenic product **6** (15%):