



Activation of Manganese Metal by a Catalytic Amount of PbCl_2 and Me_3SiCl

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Abstract: Allylation of carbonyl compounds and the Reformatsky-type reaction are performed with manganese metal which is activated by addition of a catalytic amount of Me_3SiCl and PbCl_2 in THF.

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Although manganese is a relatively abundant metal and has stronger reduction potential than zinc, it has rarely been utilized in organic synthesis except in a few cases.¹⁻⁵ One of the main reasons for this is its low reactivity toward organic compounds due to a thin but tightly bound oxide layer on its surface. From studies on activation of zinc metal for formation of alkylzinc and iodomethylzinc compounds, it was recognized that the metal-oxide coating is effectively removed by treatment with Me_3SiCl .^{6,7}

Measuring the surface of manganese metal powder by X-ray photoelectron spectroscopy (XPS), several comments can be made concerning the Mn(2p) and O(1s) peaks (Figure 1). i) When commercial manganese powder (A) was subjected to X-ray spattering for 14 min (B), broadening of two Mn peaks, Mn(2p_{1/2}) and Mn(2p_{3/2}), was observed. However, it is difficult to distinguish between Mn-Mn and Mn-O peaks presumably due to a small difference in binding energy. ii) The content of manganese oxide can be estimated by the atom ratio O / Mn, and the ratio was decreased by the spattering. iii) Treatment of manganese metal with Me_3SiCl (10 mol% of Mn) in THF at 25 °C for 1 h also resulted in a decrease of the atom ratio O / Mn (C), which suggests abstraction of oxygen atoms from the surface. The effect of the treatment corresponded to a 10 min spattering, i.e., ca. 100 nm depth.

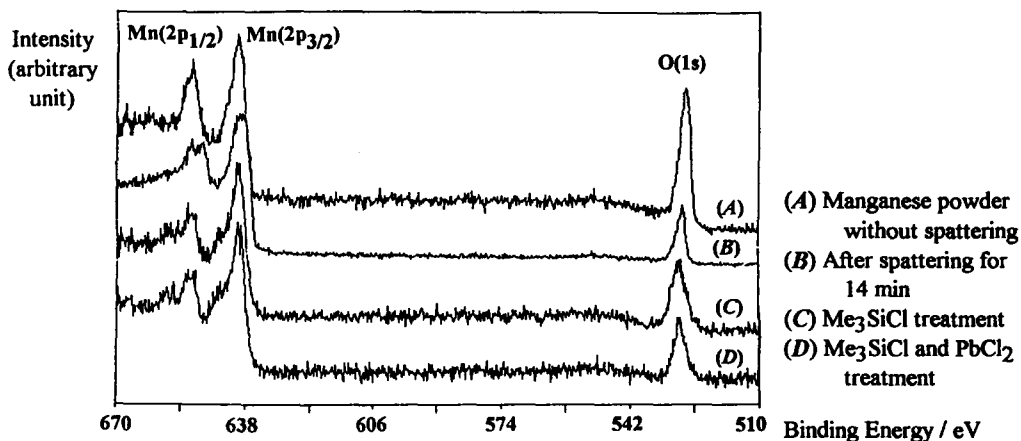
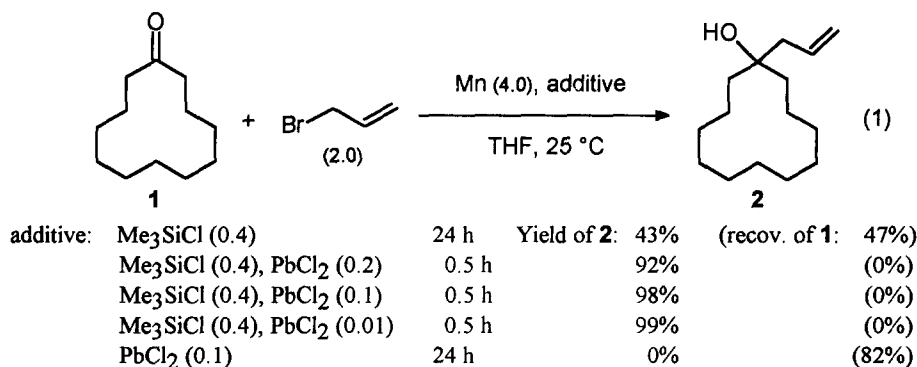


Figure 1. Measured Mn(2p) and O(1s) X-ray Photoelectron Spectra of Manganese Powder

^1H NMR analysis of a supernatant solution of the mixture of manganese powder and Me_3SiCl in $\text{THF-}d_8$ after stirring at $25\text{ }^\circ\text{C}$ for 1 h under an argon atmosphere, showed a peak of $\text{Me}_3\text{SiOSiMe}_3$.^{5c} The observation, therefore, also supports the abstraction of oxygen atoms from the surface by treatment with Me_3SiCl .

Reactivity of the activated manganese powder was checked by allylation of cyclododecanone with allyl bromide in THF as a probe.^{1,2} Treatment of cyclododecanone (**1**) with 2 equiv. of allyl bromide and 4 equiv. of manganese metal in the presence of 0.4 equiv. of Me_3SiCl at $25\text{ }^\circ\text{C}$ for 24 h, produced homoallylic alcohol **2** in 43% yield together with recovered cyclododecanone in 47% yield (eq. 1). The reaction, however, did not take place with the addition of ethereal hydrochloric acid (0.4 equiv.) instead of Me_3SiCl . In contrast, such Lewis acids (0.4 equiv.) as Et_2AlCl and $\text{BF}_3\cdot\text{OEt}_2$ accelerated the allylation and **2** was obtained in 67% and 42% yields, respectively.



Another activation method for metal powder⁸ is to add a catalytic amount of a second metal element which has weaker reduction potential.^{2,9} Thus, we further examined the addition of such a second metal to manganese powder. Among those investigated, addition of a catalytic amount of PbCl_2 to the manganese metal was found to accelerate the allylation dramatically. This effect of lead on manganese is opposite to that on zinc where a catalytic amount of lead deactivates the metal.⁶ When 0.2 equiv. of PbCl_2 was added to the reaction mixture, an exothermic reaction (ca. $40\text{ }^\circ\text{C}$) was observed and allylation of cyclododecanone was completed at $25\text{ }^\circ\text{C}$ within 30 min to give homoallylic alcohol **2** in 92% yield. The amount of PbCl_2 can be reduced to 0.25 mol% of manganese powder without any decrease of the yields. Although manganese metal can reduce Pb(II) to Pb(0) , allylation of **1** using lead powder and Me_3SiCl did not proceed at all.

The XPS spectrum of the manganese metal treated with PbCl_2 (1 mol% of Mn) and Me_3SiCl (10 mol% of Mn) in Figure 1 (*D*), showed no difference from the Me_3SiCl -treated metal (*C*). The role of lead on enhancement of the reducing ability of manganese metal, therefore, is still obscure.

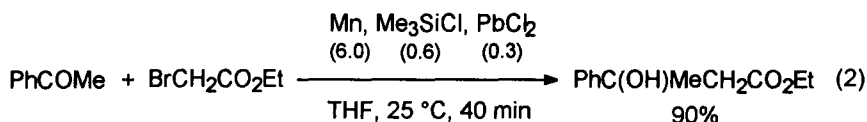
Reactions of allylic manganese reagents with several carbonyl compounds are summarized in Table 1. Both allyl bromide and chloride could be employed as allyl halides. Homoallylic alcohols were obtained in excellent yields except with prenyl bromide (run 8). In the case of crotyl bromide, yields of adducts dropped to 40–50%, thus, 3 equiv. of the reagent were used to complete the reaction (runs 6 and 7). Carbon-carbon bonds were formed at the more substituted carbons exclusively (runs 6–8). Addition of a crotylmanganese reagent to benzaldehyde gave two diastereomers in the ratio of *anti* / *syn* = 58 / 42, which is almost the same as the $\text{MnCl}_2\text{-LiAlH}_4$ reagent.¹ Chemoselective addition to an aldehyde group was also observed (run 4).²

The manganese metal activated by Me_3SiCl and PbCl_2 was also effective for the Reformatsky-type reaction (eq. 2).¹⁰ Cahiez reported a similar Reformatsky-type reaction in 1989,² which was conducted by addition of ZnCl_2 and Ac_2O in ethyl acetate at $60\text{ }^\circ\text{C}$. The latter additive, Ac_2O was mentioned to be essential to prevent the reverse reaction. The present reaction with the activated manganese, however, proceeds smoothly at $25\text{ }^\circ\text{C}$ and does not require Ac_2O .

Table 1. Addition of Allylmanganese Reagents to Carbonyl Compounds^a

run	R ¹	R ²	R ³	R ⁴	X	Time / h	Yield / % ^b
1	Ph	H	H	H	Br	0.5	98
2	Ph(CH ₂) ₂	H				1	83 ^c
3	-(CH ₂) ₁₁ -					0.5	99
4	Me	(CH ₂) ₄ CO ₂ Me				2	72
5	-(CH ₂) ₁₁ -		H	H	Cl	6	94 ^d
6	Ph	H	Me	H	Br	1.5	91 ^{e,f,g}
7	-(CH ₂) ₁₁ -					1.5	93 ^{e,f}
8	-(CH ₂) ₁₁ -		Me	Me	Br	24	6 ^{e,h}

(a) Reaction was conducted on a 1 mmol scale. Allylic halide (2.0 mmol), manganese metal (4.0 mmol), PbCl₂ (0.01 mmol) and Me₃SiCl (0.4 mmol) were employed. (b) Isolated yield. (c) Allyl bromide was added within 5 min (run 3). (d) PbCl₂ (0.2 mmol) was used and the reaction was performed at 40 °C. (e) Allylic bromide (3.0 mmol), manganese metal (6.0 mmol), PbCl₂ (0.015 mmol) and Me₃SiCl (0.6 mmol) were employed. (f) Crotyl bromide was added to the reaction mixture over a period of 1.5 h. (g) *anti* / *syn* = 58 / 42. (h) Cyclododecanone was recovered in 90% yield.



Effects of additives on the Reformatsky-type reaction were also examined (Table 2). Although β-hydroxy ester **3** was produced in 2–13% by addition of Me₃SiCl, Et₂AlCl¹¹ or BF₃·Et₂O, further addition of PbCl₂ increased the yield of **3** markedly. In contrast, addition of anhydrous hydrochloric acid was ineffective both in the presence and absence of PbCl₂.

Table 2. Effects of Additives on the Reformatsky-type Reaction^a

additive	PbCl ₂ (0.2)			none	
Me ₃ SiCl (0.4)	20 min	88%	(0%)	24 h	2% (91%)
Et ₂ AlCl (0.4)	20 min	84%	(10%)	24 h	13% (79%)
BF ₃ ·OEt ₂ (0.4)	24 h	67%	(5%)	24 h	5% (94%)
anhydrous HCl in Et ₂ O (0.4)	24 h	0%	(94%)	24 h	0% (94%)
none	24 h	0%	(93%)	24 h	0% (95%)

(a) Reaction was conducted on a 1 mmol scale. Ethyl bromoacetate (2.0 mmol) and manganese metal (4.0 mmol) were employed. Results are indicated in the following sequence: reaction time, isolated yield of **3**, (recovery of cyclododecanone (**1**)).

Typical procedure for allylation of cyclododecanone: To a mixture of manganese metal¹² (0.22 g, 4.0 mmol) and PbCl₂¹³ (2.8 mg, 0.010 mmol) in THF (4 mL) was added Me₃SiCl (0.05 mL, 0.4 mmol) at 25 °C, and the mixture was stirred at 25 °C for 30 min. A solution of cyclododecanone (1, 0.18 g, 1.0 mmol) in THF (1 mL) was added to the mixture. A solution of allyl bromide (0.24 g, 2.0 mmol) in THF (2 mL) was added to the mixture over a period of 30 min. After 30 min stirring, a THF solution of anhydrous Bu₄NF (1 M, 10 mL) was added slowly to the reaction mixture at 25 °C, and the mixture was stirred at 25 °C for an additional 1 h. The resulting mixture was extracted with ether (3x10 mL) and the organic extracts were dried over MgSO₄ and concentrated. Purification by column chromatography on silica gel (hexane-ethyl acetate, 10:1) gave 0.22 g (99% yield) of homoallylic alcohol 2.

Utilization of the novel reduction system, Mn-PbCl₂-Me₃SiCl, in organic synthesis is currently under investigation.

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- Manganese powder was purchased from two sources: Rare Metallic Co. (99% purity, -80 mesh) and Kojundo Chemical Laboratory Co. (99.9% purity, -50 mesh). The powder was used for reactions without any purification.
- Lead(II) chloride (99.99% purity) was purchased from Rare Metallic Co.

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