

## Activation of Manganese Metal by a Catalytic Amount of $\text{PbCl}_2$ and $\text{Me}_3\text{SiCl}$

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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  $\text{Me}_3\text{SiCl}$  and  $\text{PbCl}_2$  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.<sup>1-5</sup> 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  $\text{Me}_3\text{SiCl}$ .<sup>6,7</sup>

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<sub>1/2</sub>) and Mn(2p<sub>3/2</sub>), 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  $\text{Me}_3\text{SiCl}$  (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.

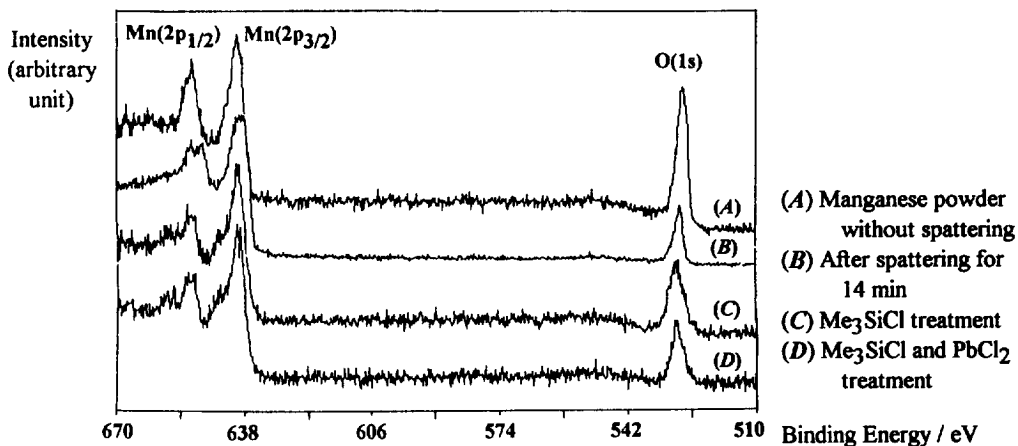
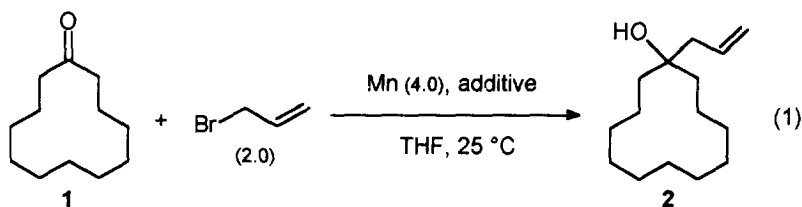


Figure 1. Measured Mn(2p) and O(1s) X-ray Photoelectron Spectra of Manganese Powder

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

Reactivity of the activated manganese powder was checked by allylation of cyclododecanone with allyl bromide in THF as a probe.<sup>1,2</sup> Treatment of cyclododecanone (**1**) with 2 equiv. of allyl bromide and 4 equiv. of manganese metal in the presence of 0.4 equiv. of  $\text{Me}_3\text{SiCl}$  at  $25^\circ\text{C}$  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  $\text{Me}_3\text{SiCl}$ . In contrast, such Lewis acids (0.4 equiv.) as  $\text{Et}_2\text{AlCl}$  and  $\text{BF}_3\cdot\text{OEt}_2$  accelerated the allylation and **2** was obtained in 67% and 42% yields, respectively.



additive:	$\text{Me}_3\text{SiCl}$ (0.4)	24 h	Yield of <b>2</b> :	43%	(recov. of <b>1</b> :	47%)
	$\text{Me}_3\text{SiCl}$ (0.4), $\text{PbCl}_2$ (0.2)	0.5 h		92%		(0%)
	$\text{Me}_3\text{SiCl}$ (0.4), $\text{PbCl}_2$ (0.1)	0.5 h		98%		(0%)
	$\text{Me}_3\text{SiCl}$ (0.4), $\text{PbCl}_2$ (0.01)	0.5 h		99%		(0%)
	$\text{PbCl}_2$ (0.1)	24 h		0%		(82%)

Another activation method for metal powder<sup>8</sup> is to add a catalytic amount of a second metal element which has weaker reduction potential.<sup>2,9</sup> Thus, we further examined the addition of such a second metal to manganese powder. Among those investigated, addition of a catalytic amount of  $\text{PbCl}_2$  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.<sup>6</sup> When 0.2 equiv. of  $\text{PbCl}_2$  was added to the reaction mixture, an exothermic reaction (ca.  $40^\circ\text{C}$ ) was observed and allylation of cyclododecanone was completed at  $25^\circ\text{C}$  within 30 min to give homoallylic alcohol **2** in 92% yield. The amount of  $\text{PbCl}_2$  can be reduced to 0.25 mol% of manganese powder without any decrease of the yields. Although manganese metal can reduce  $\text{Pb(II)}$  to  $\text{Pb(0)}$ , allylation of **1** using lead powder and  $\text{Me}_3\text{SiCl}$  did not proceed at all.

The XPS spectrum of the manganese metal treated with  $\text{PbCl}_2$  (1 mol% of Mn) and  $\text{Me}_3\text{SiCl}$  (10 mol% of Mn) in Figure 1 (D), showed no difference from the  $\text{Me}_3\text{SiCl}$ -treated metal (C). The role of lead on enhancement of the reducing ability of manganese metal, therefore, is still obscure.

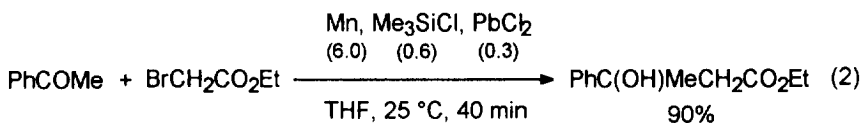
Reactions of allylic manganese reagents with several carbonyl compounds are summarized in Table 1. Both allyl bromide and chloride could be employed as allyl halides. Homoallylic alcohols were obtained in excellent yields except with prenyl bromide (run 8). In the case of crotyl bromide, yields of adducts 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.<sup>1</sup> Chemoselective addition to an aldehyde group was also observed (run 4).<sup>2</sup>

The manganese metal activated by  $\text{Me}_3\text{SiCl}$  and  $\text{PbCl}_2$  was also effective for the Reformatsky-type reaction (eq. 2).<sup>10</sup> Cahiez reported a similar Reformatsky-type reaction in 1989,<sup>2</sup> which was conducted by addition of  $\text{ZnCl}_2$  and  $\text{Ac}_2\text{O}$  in ethyl acetate at  $60^\circ\text{C}$ . The latter additive,  $\text{Ac}_2\text{O}$  was mentioned to be essential to prevent the reverse reaction. The present reaction with the activated manganese, however, proceeds smoothly at  $25^\circ\text{C}$  and does not require  $\text{Ac}_2\text{O}$ .

Table 1. Addition of Allylmanganese Reagents to Carbonyl Compounds<sup>a</sup>

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

(a) Reaction was conducted on a 1 mmol scale. Allylic halide (2.0 mmol), manganese metal (4.0 mmol), PbCl<sub>2</sub> (0.01 mmol) and Me<sub>3</sub>SiCl (0.4 mmol) were employed. (b) Isolated yield. (c) Allyl bromide was added within 5 min (run 3). (d) PbCl<sub>2</sub> (0.2 mmol) was used and the reaction was performed at 40 °C. (e) Allylic bromide (3.0 mmol), manganese metal (6.0 mmol), PbCl<sub>2</sub> (0.015 mmol) and Me<sub>3</sub>SiCl (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 Me<sub>3</sub>SiCl, Et<sub>2</sub>AlCl<sup>11</sup> or BF<sub>3</sub>·Et<sub>2</sub>O, further addition of PbCl<sub>2</sub> increased the yield of **3** markedly. In contrast, addition of anhydrous hydrochloric acid was ineffective both in the presence and absence of PbCl<sub>2</sub>.

Table 2. Effects of Additives on the Reformatsky-type Reaction<sup>a</sup>

additive	PbCl <sub>2</sub> (0.2)		none	
	Time	Yield (%)	Time	Yield (%)
Me <sub>3</sub> SiCl (0.4)	20 min	88% (0%)	24 h	2% (91%)
Et <sub>2</sub> AlCl (0.4)	20 min	84% (10%)	24 h	13% (79%)
BF <sub>3</sub> ·OEt <sub>2</sub> (0.4)	24 h	67% (5%)	24 h	5% (94%)
anhydrous HCl in Et <sub>2</sub> 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 metal<sup>12</sup> (0.22 g, 4.0 mmol) and PbCl<sub>2</sub><sup>13</sup> (2.8 mg, 0.010 mmol) in THF (4 mL) was added Me<sub>3</sub>SiCl (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 Bu<sub>4</sub>NF (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 (3×10 mL) and the organic extracts were dried over MgSO<sub>4</sub> 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-PbCl<sub>2</sub>-Me<sub>3</sub>SiCl, in organic synthesis is currently under investigation.

#### ACKNOWLEDGMENT

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- Lead(II) chloride (99.99% purity) was purchased from Rare Metallic Co.