

# A Dramatic Effect of a Catalytic Amount of Lead on the Simmons-Smith Reaction and Formation of Alkylzinc Compounds from Iodoalkanes. Reactivity of Zinc Metal: Activation and Deactivation

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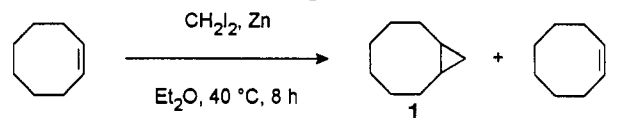
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**Summary:** A trace amount of lead found in zinc derived from the pyrometallurgy smelting method decreases the reactivity of zinc toward diiodomethane and iodoalkanes substantially, and this negative effect can be suppressed by the addition of a catalytic amount of  $\text{Me}_3\text{SiCl}$ .

Zinc metal is used as a reducing agent in many reactions, such as the Reformatsky reaction,<sup>1</sup> the Simmons-Smith reaction,<sup>2</sup> and the preparation of alkylzinc compounds from iodoalkanes.<sup>3</sup> However, the reactions are not always reproducible, and various zinc activation methods<sup>4-7</sup> have been reported to overcome the difficulty. Because the surface of zinc is covered with a thin layer of zinc oxide (*vide infra*), the simplest activation is achieved by the removal of the oxide layer by washing with mineral acids.<sup>4</sup> A zinc-copper or zinc-silver couple is frequently employed when the reaction does not proceed adequately.<sup>5</sup> These studies have focused on how to obtain activated zinc metal, and therefore, the problem of the capricious reactivity of zinc has remained. We disclosed herein (i) that pure zinc powder is sufficiently active if the oxide layer on the surface is removed, (ii) that contamination with a trace amount of lead, which is present in zinc derived from the pyrometallurgy smelting method, markedly inhibits the progress of the Simmons-Smith reaction and the formation of alkylzinc compounds, and (iii) that addition of a catalytic amount of  $\text{Me}_3\text{SiCl}$  to a zinc suspension suppresses the effect of the lead and, moreover, accelerates the reduction of diiodomethane and iodoalkanes with zinc.

**Table 1.** Simmons-Smith Reaction of Cyclooctene with Various Samples of Zinc<sup>a</sup>



run	source of zinc	content of lead <sup>b</sup> (mol % of zinc)	additive <sup>c</sup>	yield <sup>d</sup> (%)	recovery <sup>d</sup> (%)
1	Aldrich Chemical	0	none	96	2
2	E. Merck	0	none	96	2
3	Rare Metallic	0	none	89	5
4	Wako Pure Chemical	0.04	none	7	91
5	Nacalai Tesque	0.06	none	2	96
6	Kanto Chemical	0.07	none	1	95
7	E. Merck	0	Pb	20	80
8	E. Merck	0	Pb, $\text{Me}_3\text{SiCl}$	97	2
9	E. Merck	0	Pb, $\text{Et}_2\text{AlCl}$	2	90
10	Wako Pure Chemical	0.04	$\text{Me}_3\text{SiCl}$	92	2
11	Wako Pure Chemical	0.04	$\text{Et}_2\text{AlCl}$	1	93

<sup>a</sup> A mixture of cyclooctene (1.0 mmol),  $\text{CH}_2\text{I}_2$  (2.0 mmol), and zinc (4.0 mmol) in ether (0.65 mL) was stirred at 40 °C for 8 h. <sup>b</sup> Amount of lead in zinc powder was measured by fluorescent X-ray and elementary analysis. <sup>c</sup> 0.5 mol % (0.02 mol) of lead, 2 mol % (0.08 mmol) of  $\text{Me}_3\text{SiCl}$ , and/or 2 mol % (0.8 mmol) of  $\text{Et}_2\text{AlCl}$  were employed. <sup>d</sup> Yields were determined by GLPC.

There are two kinds of zinc powder available: electrolytic zinc derived by hydrometallurgy and distilled zinc derived by pyrometallurgy. They are produced by different smelting methods, and thus, their purities, especially their lead contents, are quite different. Fluorescent X-ray and elementary analyses revealed that electrolytic zinc is pure and free of lead, while the distilled zinc contained ca. 0.04–0.07 mol % of lead.

When the Simmons-Smith reaction<sup>4</sup> was carried out with several samples of zinc powder,<sup>8</sup> the progress of the reaction was found to be heavily dependent on the nature of the zinc (Table 1). For example, cyclopropanation of cyclooctene proceeded smoothly at 40 °C within 8 h with pure electrolytic zinc, such as the Aldrich Chemical (99.998% on the label), E. Merck (>95%), and Rare Metallic (99.999%) reagents (runs 1–3). Cyclooctene and diiodomethane remained almost unchanged with the distilled zinc purchased from Wako Pure Chemical (>90%), Nacalai Tesque (>90%), and Kanto Chemical (>90%) (runs 4–6).

The above cyclopropanation of cyclooctene was found to be suppressed by the addition of 0.5 mol % of lead powder<sup>9</sup> to pure electrolytic zinc (run 7), but to a lesser

(8) Zinc powder was simply washed several times with 5% hydrochloric acid, washed in turn with water, methanol, and ether, and dried *in vacuo* according to ref 4a. The zinc powder was stored under an argon atmosphere. We employed this hydrochloric acid-washed zinc powder in all reactions unless otherwise noted.

(9) Lead powder (99.999% purity) was purchased from Rare Metallic Co., Japan.

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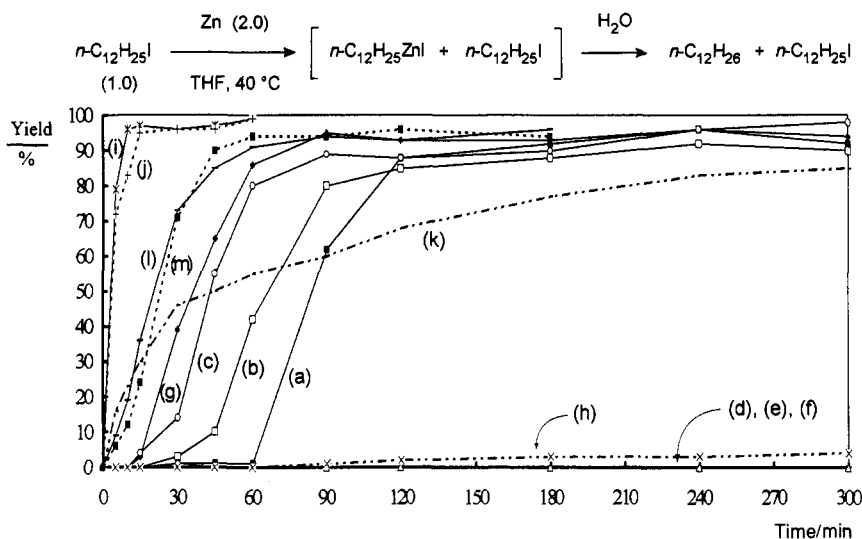
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**Figure 1.** Formation of dodecylzinc iodide by using various samples of zinc: (a) Aldrich, (b) Merck, (c) Rare Metallic, (d) Wako, (e) Nacalai, (f) Kanto, (g) Merck ( $\text{Me}_3\text{SiCl}$  wash), (h) Merck ( $\text{Me}_3\text{SiCl}$  wash) + Pb, (i) Merck +  $\text{Me}_3\text{SiCl}$ , (j) Merck + Pb +  $\text{Me}_3\text{SiCl}$ , (k) Wako +  $\text{Me}_3\text{SiCl}$ , (l) Merck +  $\text{Et}_2\text{AlCl}$ , (m) Merck + Pb +  $\text{Et}_2\text{AlCl}$ .

extent than when the distilled zinc was employed, in spite of the high lead content. Auger electron spectroscopy (AES) of the distilled zinc proved that the lead was not localized on the surface of the zinc. Because a small amount of lead does not form a solid solution with zinc,<sup>10</sup> the lead in distilled zinc precipitates as fine particles of metallic lead in a zinc matrix<sup>11</sup> or it forms a supersaturated solid solution with zinc, depending on the rate of cooling. The different negative effects could stem from the character of the lead.

The  $^1\text{H}$  NMR spectrum of the supernatant of the reaction mixture of diiodomethane and pure zinc in ether at  $40^\circ\text{C}$  for 2 h showed a singlet at  $\delta$  1.40 (in acetone- $d_6$ ) assigned to the zinc-carbenoid  $\text{ICH}_2\text{ZnI}$  (or  $(\text{ICH}_2)_2\text{Zn/ZnI}_2$ ).<sup>12</sup> Meanwhile, the supernatant of the reaction mixture employing zinc and lead (5 mol % of zinc) revealed that diiodomethane remained unchanged.<sup>13</sup> When the same amount of lead powder was added to the filtered solution of the zinc-carbenoid prepared with pure zinc, cyclopropane **1** was produced after stirring at  $40^\circ\text{C}$  for 2 h without any decrease in yield. These results suggest that the lead affects the initial reduction step of the diiodomethane/zinc reaction.

A similar zinc deactivating effect by a catalytic amount of lead was observed in a simple reduction of an iodoalkane to an alkylzinc iodide (Figure 1).<sup>3</sup> Although the induction periods varied with the samples, dodecylzinc iodide was produced from 1-iodododecane and pure electrolytic zinc in over 90% yield after being stirred at  $40^\circ\text{C}$  for 3 h.<sup>14,15</sup> In contrast, 1-iodododecane was recovered almost quan-

titatively upon using distilled zinc. The high reactivity of electrolytic zinc was first observed in 1962 by Gaudemar in the preparation of allylzinc bromide.<sup>16</sup> In 1988, Knochel employed zinc dust (99.99% purity) for the preparation of alkylzinc compounds.<sup>3c,17</sup> The high reactivity of electrolytic zinc for the reduction of iodoalkanes may stem from the absence of lead. Indeed, formation of dodecylzinc iodide was suppressed completely for 12 h by the addition of 0.5 mol % of lead to pure zinc (Figure 1).<sup>18</sup> Addition of other metals, such as gold, silver, copper, tin, aluminum, niobium, and bismuth, did not disturb the formation of alkylzinc; dodecylzinc iodide was produced quantitatively after the mixture was stirred at  $40^\circ\text{C}$  for 4 h.

Analysis by AES showed that the surface of all zinc powders was covered with a thin layer of zinc oxide (Figure 2). The thickness of the layer varied, but on average, the oxide layer on the lead-containing zinc was thicker than that on the pure zinc. Treatment of zinc powder with aqueous hydrochloric acid<sup>4</sup> eliminated the oxide layer considerably, but it was not sufficient. The thickness of the oxide layer did not change after ultrasonic irradiation for 2 h. Treatment with  $\text{Me}_3\text{SiCl}$ <sup>17,19</sup> or  $\text{Et}_2\text{AlCl}$ <sup>20</sup> in THF for 15 min was effective in removing the oxide layer.

When pure zinc powder pretreated with  $\text{Me}_3\text{SiCl}$  (5 mol % of zinc) was employed for the formation of dodecylzinc iodide, the induction period became shorter, as we ex-

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(11) A small amount of lead (ca. 0.5 mol %) in distilled zinc derived from the ISP smelting method precipitated as fine particles of metallic lead into the zinc matrix, which was observed by electron microscope and EPMA (the data were given by Mr. Tooru Oshita).

(12) Denmark, S. E.; Edwards, J. P.; Wilson, S. R. *J. Am. Chem. Soc.* 1992, 114, 2592–2602 and references cited therein.

(13) The results show sharp contrast to the same reduction in THF, where further reduction of zinc-carbenoid,  $\text{ICH}_2\text{ZnI}$ , to a geminal dizinc compound,  $\text{CH}_2(\text{ZnI})_2$ , proceeds smoothly at room temperature.

(14) Typical procedure: To a mixture of zinc (10 mmol) in THF (5 mL) was added 1-iodododecane (5.0 mmol) at  $25^\circ\text{C}$ , and then the mixture was warmed to  $40^\circ\text{C}$ . The amount of dodecylzinc iodide was estimated by measurement of dodecane by GLPC after quenching a small aliquot of the mixture with water.

(15) Iodinolysis of the reaction mixture was conducted to check the amount of active dodecylzinc iodide. Reaction conditions in Figure 1, reaction time, and yields of  $n\text{-C}_{12}\text{H}_{25}\text{I}$  and  $n\text{-C}_{12}\text{H}_{26}$  are as follows: (b) Merck, 3 h, 90% and 9%; (i) Merck +  $\text{Me}_3\text{SiCl}$ , 1 h, 88% and 5%; (j) Merck + Pb +  $\text{Me}_3\text{SiCl}$ , 1 h, 90% and 4%.

(16) Gaudemar, M. *Bull. Soc. Chim. Fr.* 1962, 974–987. For use of reactive zinc produced *in situ* by electrolysis, see: Tokuda, M.; Miura, N.; Karasawa, T.; Fujita, H.; Siginome, H. *Tetrahedron Lett.* 1993, 34, 7607–7610.

(17) Recently, Knochel used the zinc dust purchased from Aldrich (–325 mesh)<sup>3c</sup> and activated it with 1,2-dibromoethane and  $\text{Me}_3\text{SiCl}$ . He also mentioned the accelerating effect of  $\text{Me}_3\text{SiCl}$  for the preparation of butylzinc iodide in the footnote of ref 3c. For activation of zinc with  $\text{Me}_3\text{SiCl}$ , see: Picotin, G.; Miginiac, P. *J. Org. Chem.* 1987, 52, 4796–4798.

(18) Dodecylzinc iodide was produced in 82% after 30 h of stirring at  $40^\circ\text{C}$  in the case of a mixture of pure zinc and 5 mol % of lead. The result shows sharp contrast to the distilled zinc, where 1-iodododecane still remained after exposure at  $40^\circ\text{C}$  for 30 h.

(19) Formation of  $\text{Me}_3\text{SiOSiMe}_3$  was observed by  $^1\text{H}$  NMR analysis of the supernatant of the mixture of  $\text{Me}_3\text{SiCl}$  and zinc in THF- $d_6$ .

(20) Maruoka, K.; Hashimoto, S.; Kitagawa, Y.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* 1977, 99, 7705–7707.

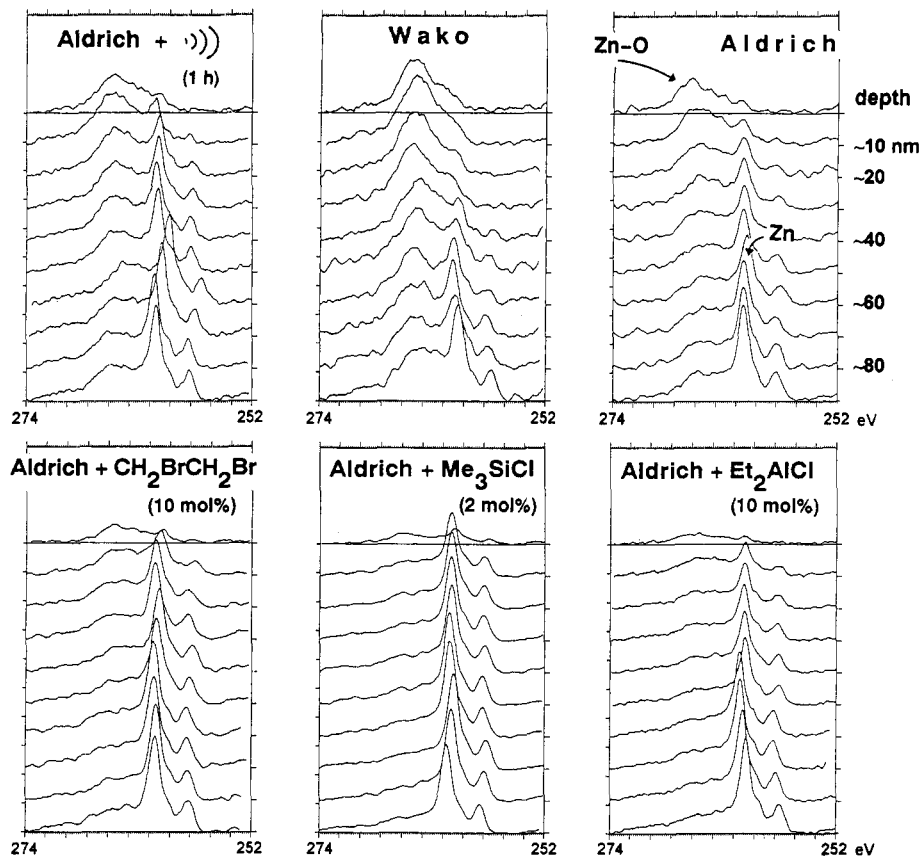


Figure 2. Auger electron spectroscopic data (Zn LMM) of several samples of zinc powder after activation.

pected. However, by inclusion of a catalytic amount of lead, dodecylzinc iodide was not produced with the  $\text{Me}_3\text{SiCl}$ -pretreated zinc, even at 40 °C for 5 h. Since the thickness of the zinc oxide layer did not increase during the mixing of the pure zinc and the lead powder (5 mol % of zinc) in THF at 25 °C for 1 h, this is not responsible for the deactivating effect of lead.

Unlike when using  $\text{Me}_3\text{SiCl}$  pretreated zinc, the addition of the same catalytic amount of  $\text{Me}_3\text{SiCl}$  at the reduction stage of 1-iododecane accelerated the reaction markedly both in case of the lead-containing distilled zinc and the case of pure electrolytic zinc to which a catalytic amount of lead was added.<sup>15</sup> The negative effect of lead on the Simmons–Smith reaction was also diminished by addition of  $\text{Me}_3\text{SiCl}$  (Table 1, runs 8 and 10). Although the addition of  $\text{Et}_2\text{AlCl}$  accelerated the reduction of 1-iododecane with zinc in the presence of lead,<sup>21</sup> it was not effective for the Simmons–Smith reaction.

(21) The different accelerating effects of  $\text{Me}_3\text{SiCl}$  and  $\text{Et}_2\text{AlCl}$  suggest that  $\text{Me}_3\text{SiCl}$  does not function only as a Lewis acid.

The mechanism of the deactivating effect of lead on the reduction of iodoalkanes with zinc is not clear; however, it is significant that the trace of lead that is contained in distilled zinc influences the popular zinc-mediated reactions.

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