



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at [http://www.nap.edu/catalog.php?record\\_id=12654](http://www.nap.edu/catalog.php?record_id=12654)). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

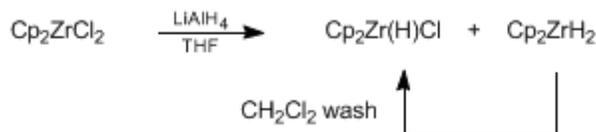
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*September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 9, p.162 (1998); Vol. 71, p.77 (1993).*

## SCHWARTZ'S REAGENT

### [Zirconium, chlorobis( $\eta^5$ -2,4-cyclopentadien-1-yl)hydro-]



Submitted by Stephen L. Buchwald<sup>1</sup>, Susan J. LaMaire, Ralph B. Nielsen, Brett T. Watson, and Susan M. King.

Checked by Daniel J. Keavy and Robert K. Boeckman, Jr..

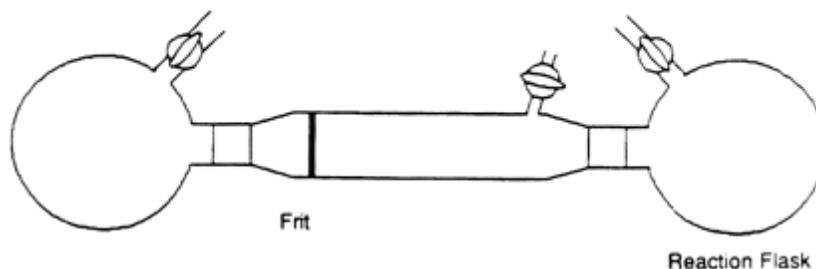
### 1. Procedure

*CAUTION! The washing procedure described in (Note 8) should be followed carefully. On one occasion, allowing a contact time of ca. 1 hr while attempting to use a cannula filter to remove the methylene chloride led to an exothermic decomposition reaction.*

To a dry, 1-L Schlenk flask equipped with a magnetic stirring bar is added under argon zirconocene dichloride (100 g, 0.342 mol) (Note 1), followed by dry tetrahydrofuran (650 mL) (Note 2). Dissolution of the solid is accomplished by gentle heating with a heat gun. To the solution at  $\sim 35^\circ\text{C}$  (Note 3) is added dropwise, over a 45-min period, a filtered solution (Note 4),(Note 5) of lithium aluminum hydride (3.6 g, 94 mmol) (Note 4) in ethyl ether (100 mL) (Note 6),(Note 7). The resulting suspension is stirred at room temperature for 90 min. The mixture is then Schlenk-filtered (Figure 1) under argon using a "D" frit. The resulting white solid is washed with tetrahydrofuran ( $4 \times 75$  mL), methylene chloride ( $2 \times 100$  mL) (Note 8) with stirring or agitation of the stirbar immersed in the slurry, and then with ether ( $4 \times 50$  mL). The resulting white solid is dried under reduced pressure to give a white powder (Note 9), 66 g, 75% yield (Note 10).

Figure 1

To Argon/Vacuum

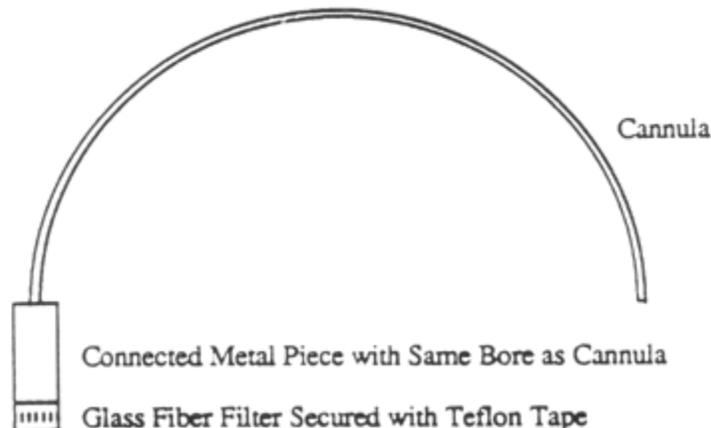


### 2. Notes

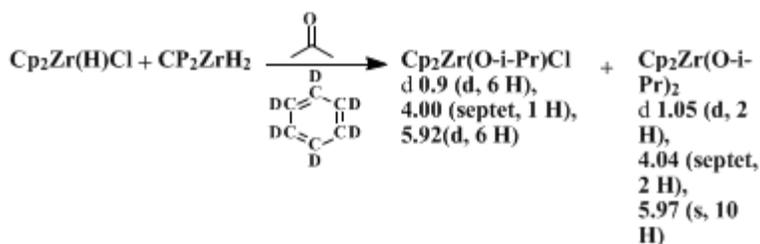
1. Zirconocene dichloride is purchased from Boulder Scientific Co., and used without any further purification.
2. Tetrahydrofuran is distilled from sodium/benzophenone ketyl under argon at atmospheric pressure immediately before use.
3. Crystallization occurs if the temperature is allowed to fall below  $35^\circ\text{C}$ . The reaction can be conducted successfully even if a small amount of solid forms.
4. This solution is prepared by adding lithium aluminum hydride to ethyl ether, stirring the suspension for 10 min, and allowing the undissolved material to settle to the bottom of the flask. The clear solution is then filtered under argon using a modified cannula (Figure 2) fitted with a piece of glass fiber filter

(Number 34 Glass, 24 mm, purchased from Schleicher & Schuell); a Schlenk-filtered or commercial clear solution would work as well.

**Figure 2**



5. **Lithium aluminum hydride** (95%) is purchased from Alfa Products, Morton/Thiokol, Inc.
6. A slightly exothermic reaction results that maintains the temperature of the reaction mixture at  $\sim 35^{\circ}\text{C}$  during the addition.
7. **Ethyl ether** is distilled from **sodium/benzophenone ketyl** under **argon** at atmospheric pressure immediately before use.
8. **Methylene chloride** is distilled from **calcium hydride** under **argon** at atmospheric pressure immediately before use. It is important to keep the **methylene chloride** wash in contact with the Schwartz's Reagent for a maximum period of 10 min; use of a frit filter is essential.
9. Schwartz's Reagent is an air, moisture, and moderately light sensitive compound that should be dried in the dark, and protected from moisture and light during storage.
10. A small sample of the hydride is suspended in benzene- $d_6$  and assayed in a 5-mm NMR tube by treatment with a known amount of excess **acetone** (Equation 1). The relative areas of the signal for the mono- and diisopropoxides are determined by  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$  integrating the methyl doublets):  $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ : 94–96%,  $\text{Cp}_2\text{ZrH}_2$ : 4–6%.<sup>2</sup>



### Waste Disposal Information

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

### 3. Discussion

Schwartz's Reagent<sup>3</sup> is available commercially (from the Aldrich Chemical Company, Inc.) although it is quite expensive. Two literature preparations of this important reagent are available. The first utilizes  $\text{LiAl}(\text{OtBu})_3\text{H}$  to reduce zirconocene dichloride.<sup>4,5</sup> The second method utilizes **sodium bis (2-methoxyethoxy) aluminum hydride** (RED-AL) as the reducing agent.<sup>2</sup> The disadvantages of these procedures have been discussed.<sup>3</sup>

Wailes, in his original report on the preparation of  $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ , investigated the **lithium aluminum hydride** reduction of zirconocene dichloride and found that this leads to considerable overreduction to

give Cp<sub>2</sub>ZrH<sub>2</sub>.<sup>4,5</sup> Later it was found that treatment of Cp<sub>2</sub>ZrH<sub>2</sub> with [methylene chloride](#) converts the dihydride into Schwartz's Reagent.<sup>3</sup>

In the procedure described here, zirconocene dichloride is reduced to a mixture of Cp<sub>2</sub>Zr(H)Cl, and Cp<sub>2</sub>ZrH<sub>2</sub> using a solution of [lithium aluminum hydride](#). Washing the mixture with [methylene chloride](#) converts the Cp<sub>2</sub>ZrH<sub>2</sub> into the desired Cp<sub>2</sub>Zr(H)Cl. This method circumvents the need for expensive reducing agents and the use of the filtered [lithium aluminum hydride](#) solution substantially simplifies the product isolation. The procedure can be performed in 3–4 hr and does not require the use of a glove box thus making it an experimentally simple, inexpensive preparation for large scale batches of Schwartz's Reagent.

The utility of Cp<sub>2</sub>ZrHCl for hydrozirconation was discovered by Schwartz.<sup>2,6 7 8 9</sup> Many subsequent applications of this useful reagent have been documented.<sup>10</sup> One such application is illustrated in the conjugate addition of a vinylzirconium reagent to form [3-\(1-octen-1-yl\)cyclopentanone](#).<sup>11</sup> In some cases Schwartz's Reagent (or its equivalent) can be prepared and used in situ.<sup>12</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 9, 143](#)
- [Org. Syn. Coll. Vol. 9, 640](#)

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## References and Notes

1. Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.
2. Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521;
3. Buchwald, S. L.; LaMaire, S. J.; Nielsen, R. B.; Watson, B. T.; King, S. M. *Tetrahedron Lett.* **1987**, *28*, 3895.
4. Wailes, P. C.; Weigold, H. *J. Organomet. Chem.* **1970**, *24*, 405;
5. Wailes, P. C.; Weigold, H. *Inorg. Synth.* **1979**, *19*, 223.
6. Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc.* **1974**, *96*, 8115;
7. Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333;
8. Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679;
9. Bertelo, C. A.; Schwartz, J. *J. Am. Chem. Soc.* **1976**, *98*, 262.
10. Negishi, E.-i.; Takahashi, T. *Aldrichimica Acta* **1985**, *18*, 31 and references therein.
11. [Chu Sun, R.; Okabe, M.; Coffen, D. L.; Schwartz, J. \*Org. Synth., Coll. Vol. IX\* \*\*1998\*\*, 640.](#)
12. Negishi, E.-i.; Miller, J. A.; Yoshida, T. *Tetrahedron Lett.* **1984**, *25*, 3407.

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## Appendix

### Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

benzophenone ketyl

SCHWARTZ'S REAGENT

Zirconium, chlorobis(η<sup>5</sup>-2,4-cyclopentadien-1-yl)hydro-

zirconocene dichloride

Cp<sub>2</sub>Zr(H)Cl

$\text{Cp}_2\text{ZrH}_2$

$\text{Cp}_2\text{ZrHCl}$

ether,  
ethyl ether (60-29-7)

acetone (67-64-1)

sodium (13966-32-0)

methylene chloride (75-09-2)

Tetrahydrofuran (109-99-9)

lithium aluminum hydride (16853-85-3)

argon (7440-37-1)

calcium hydride (7789-78-8)

sodium bis(2-methoxyethoxy) aluminum hydride

3-(1-Octen-1-yl)cyclopentanone (64955-00-6)