



## IMPORTANT: Read Before using Rieke® Zinc Guide to Handling Rieke Zinc in THF

### Introduction

Rieke® Zinc is highly reactive and is moisture and oxygen sensitive. Therefore, it is important to exclude atmospheric moisture and oxygen from the reactions. This guide contains the bare minimum amount of knowledge required to use Rieke® Zinc. If one is unfamiliar with inert atmosphere techniques, we strongly advise consulting a definitive source on the manipulation of air sensitive reagents before using this metal. Once inert atmosphere techniques are mastered, Rieke® Zinc can be successfully and easily applied to many new synthetic strategies.

### Inert Atmosphere Manipulations

The minimum equipment necessary for using Rieke® Zinc includes an argon or nitrogen source (best results are obtained using high quality nitrogen or argon), a flask equipped with a sidearm to which a septum can be attached, and cannula needles. However, a tank of nitrogen or argon with a regulator is sufficient to utilize the active zinc. It is desirable but not necessary that a manifold with both argon, or nitrogen, and vacuum source be used.

Cannula needles should be stored in an oven until needed. All equipment should be pre-dried in an oven at 125°C overnight and removed just before use. If a manifold with inert gas and vacuum sources is available, achieving an inert atmosphere is simple. The assembled glassware is attached to the manifold and vacuumed and refilled with argon or nitrogen three times. The system will then be under a suitable inert atmosphere. If no source of vacuum is available, assemble the glassware and purge it for a least 15-20 min with inert gas. To purge the system, use a long needle attached via rubber tubing to the inert gas source of argon or nitrogen from a cylinder equipped with a regulator adjusted at three to five psi. Pierce the septum to add inert gas to the reaction vessel. Insert another needle in the same septum to allow an outlet for the gas.

### Cannula Transfer of Rieke® Zinc in THF

To perform a cannula transfer from a reagent bottle, purge the flushing needle with inert gas. The bottle should be inverted and shaken vigorously several times and pressurized by inserting the flushing needle. The cannula needle is inserted into the cap and the inert gas is allowed to flush the cannula for 1-2 min.



Always make sure the cannula is stored in an oven until just prior to use. Once the cannula has been flushed with inert gas, the other end of the cannula needle can be inserted through a septum on the reaction vessel.

Two methods may be used to lower the inert gas pressure on the reaction vessel, allowing the reagent to be transferred. One method is to use the vacuum line on the manifold to decrease the system pressure slightly. The second method is to close the inert gas source on the manifold and pierce a second needle through the septum on the reaction flask, thus reducing the gas pressure.

Once the gas pressure in the reaction vessel has been slightly reduced, the cannula needle can be lowered into the reagent. This should start the flow of the Rieke® Zinc slurry into the reaction vessel. During the transfer, gently swirl the reagent bottle to allow the Rieke® Zinc to become uniform in the THF. The recommended size of cannula for the transfer of Rieke® Zinc is 14 gauge or larger. Measuring the amount of reagent in a cannula transfer is easily accomplished by reading the volume mark on the reagent bottle.

After the required amount of the reagent has been transferred, pull the cannula needle above the reagent level, but do not remove it entirely. Once the reagent is no longer coming out of the cannula, remove the cannula first from the reaction flask, then from the reagent bottle, and finally remove the inert gas flask under positive inert gas pressure.

#### **Clean-up of excess Rieke® Zinc**

Extra care must be taken when cleaning equipment containing TRACE AMOUNTS of active zinc. All operations must be performed in an efficient fume hood. Wash with isopropanol first, followed by water, and then carefully add dilute (3M) HCl. For destroying LARGE AMOUNTS of active zinc, isopropanol is added and stirred overnight followed by water, and then dilute HCl.

#### **Preparation of Organozinc Reagents Using Rieke® Zinc and Halides**

Most primary alkyl bromides react with Rieke zinc in 3-4 hours. This can be shortened considerably by refluxing. In most cases, 1.05-1.20 equivalent of Rieke® Zinc to 1.0 equivalent of alkyl halide is sufficient to achieve complete conversion to the organozinc. Secondary and tertiary alkyl bromides react with Rieke® Zinc quickly at room temperature using 1.0 equivalent of halide to 1.05-1.10 equivalent of Rieke® Zinc. Aryl iodides are also readily converted to the organozinc reagents. Generally, 1.5 equivalent of Rieke® Zinc will effect complete conversion overnight at room temperature or 1-2 hours under refluxing conditions. Aryl bromides are more difficult and require 2-3 equivalents of zinc and refluxing for 2-3 hours.



## References

1. Shriver, D.F. "The Manipulation of Air-sensitive Compounds"; McGraw-Hill Book Company; New York, N.Y. 1969.
2. Rieke, R.D. *Crit. Rev. Surface Chem* **1991**, 131.
3. Rieke, R.D. *Science* **1989**, 246, 1260

## Disclaimer

The information in this guide is presented to assist you in evaluating Rieke Metals' products. This guide and materials supplied by Rieke Metals are intended solely for use by technically qualified persons. We do not guarantee favorable results, and we assume no liability in connection with their use. This information is not intended as a license to operate under, or a recommendation to infringe upon any patent covering any material or use. This product is for research and not for drug, household or other uses.

Rieke Metals, LLC warrants that its products conform to the information contained in this and other Rieke Metals, LLC publications. The purchaser must determine the suitability of the product for its particular use.