

## **Standard Operating Procedure on the use of air/moisture sensitive chemicals in ABB467**

Background: Sensitive chemicals are usually obtained in septa sealed, Aldrich “sure seal” bottles or metal cylinders which allows their use without contamination by oxygen and moisture. Metal cylinders should be connected to a septa-inlet adaptor before use as described below.

Compounds which are handled in this way include:

- Organometallics, such as methyl lithium, butyl lithium, sec-butyl lithium, tert-butyl lithium, diethylzinc, dimethylzinc, trimethyl aluminium and any Grignard reagent.
- Mono-, di- or trialkylphosphines, mono- or diaryl phosphines
- Compounds very sensitive to hydrolysis, such as titanium tetrachloride, boron trifluoride.
- Anhydrous solvents (CHCl<sub>3</sub>, Dioxane, DMF, DMSO, MeOH, Pyridine, Et<sub>3</sub>N).
- Hydrides such as LiAlH<sub>4</sub>, Dibal-H, NaH, LiH, CaH<sub>2</sub>
- Bases such as LiHMDS, NaHMDS, KHMDS, LDA

Ordering: Ordering of any air-moisture sensitive material requires Dr. McNulty's approval. If an older container of the same material is presently in the laboratory, it must be properly disposed of first. It is everybody's responsibility to make sure that redundant sure-seal containers of sensitive and/or pyrophoric materials do not accumulate in the lab. The laboratory inventory list should be updated if a new material is ordered.

General Use and Storage: Frequent use of septa-seal bottles can damage the septa which can result in decomposition of the compound. Care should be taken in opening, using and re-sealing the septa to avoid damage to the integrity of the container. Bottles should be firmly closed, however Aldrich sure-seal screw caps can shatter if too much force is used to tighten. Once closed, the bottled should be carefully sealed with a ribbon of parafilm ensuring a tight seal around the glass and cap. Bottles should be stored in the refrigerator.

Handling of Septa-sealed and Aldrich SureSeal bottles.

Working alone in the laboratory is prohibited at any time. If you are contemplating using a pyrophoric material, even during normal work hours, ensure that a co-worker is aware of the material and when you will be using it. All pyrophoric materials should be handled in the fume hood or glovebox. In addition to safety goggles, gloves and a lab coat must be worn while using these materials. The fume hood sash should be lowered as far as possible while using. The bottle should be clamped to a ring stand or solid frame. See the attached Aldrich guide to sure seal bottles, in particular Figure 7 shows a common situation. It is advisable to actually clamp the bottle to a stand rather than simply sitting inside of a ring clamp. Make sure that there are no other flammable materials such as other solvents, chemicals or paper in the fume hood. If the compound has been stored in the fridge, allow to warm to room temp. before using. For positive pressure, rather than

attaching to a nitrogen or argon manifold, use a balloon filled with the smallest volume of argon or nitrogen that is necessary for your transfer. Always make sure that the syringe and needle you use to take out the chemical are dry and that the syringe was flushed with argon/nitrogen several times immediately prior to use. Disposable plastic syringes and needles are sufficiently dry, provided that they are only unwrapped immediately prior to use. Attach the balloon and needle to the clamped flask. Using the syringe, pull the plunger at 90 degrees from your angle of view. Never pull the syringe plunger towards yourself. Alternatively, the material can be transferred via a double-tipped needle to a separate septa-sealed flask as shown in Figure 10 in the attached Aldrich guide (note the bottle must be clamped down as before). Never "return" any unused material to the septa or sure-seal container. Small amounts of excess reagent should be quenched dropwise into a dry-ice isopropanol slurry at  $-78\text{ C}$  under argon or nitrogen. Any residue in the syringe or needle used should also be quenched in this manner. Do not place any syringe/needle aside to be cleaned up at a "later time". It is easy to forget the contents especially if multiple transfers are being done. Glassware is best cleaned up within a few seconds of use. I.e perform the transfer, then quench excess reagent and clean syringe/needle assembly into a pre-assembled dry ice slurry. Remove the balloon-needle from the bottle as soon as possible after the transfer and re-cap and seal the bottle before replacing in the refrigerator as described above.

#### Use of dry metal hydrides such as $\text{LiAlH}_4$ , $\text{NaH}$ , $\text{CaH}_2$

Many metal hydrides can be obtained either as solutions in organic solvent in septa or sure-seal bottles, which should be handled as described above, or as dry solids or oil dispersions. Dry metal hydrides such as  $\text{LiAlH}_4$  or  $\text{LiH}$  (etc) should be weighed directly into a tared flask under dry argon or nitrogen, capped immediately and re-weighed. They should NEVER be weighed out onto weigh-paper or any other media directly. It is always best to weigh such materials as the limiting reagent first and modify equivalents of other materials in the reaction accordingly. This avoids topping up, or removing pyrophoric hydrides from the reaction vessel or container.