NJIT New Jersey Institute of Technology

PYROPHORIC ORGANOLITHIUM REAGENTS

STANDARD OPERATING PROCEDURE

Type of SOP: ☐ Process ☐ Hazardous Chemical ☐ Hazard Class

Department: _____ **Building:** _____ **Room #:**_____

Principal Investigator: _____ **Phone #:**_____

Prepared By: _____ **Email:** _____ **Date:** _____

1. HAZARD OVERVIEW

This procedure will cover the storage, transfer and use of organolithium reagents including, but not necessarily limited to, the materials listed the Appendix. In general, the primary hazard of the materials are that they ignite spontaneously when exposed to air. These pyrophoric properties requires them to be handled carefully to exclude them from air/moisture. Additionally, they all tend to be toxic and come dissolved in a flammable solvent. Other common hazards include corrosivity, teratogenicity, water reactivity, peroxide formation, along with damage to the liver, kidneys, and central nervous system.

2. PERSONAL PROTECTIVE EQUIPMENT (PPE)

At minimum, safety glasses, lab coats, and gloves are required. Additional or more protective PPE may be required.

- Gloves must be worn when handling pyrophoric chemicals. Nitrile gloves should be adequate for handling most of these in general laboratory settings, but they are combustible. Be sure to use adequate protection to prevent skin exposures. Sigma-Aldrich recommends the use of nitrile gloves underneath neoprene gloves.
- Flame-resistant gloves are also available for purchase, but are generally not used due to their poor dexterity when doing delicate chemical transfer work.
- **A lab coat or apron, not made from easily ignited material like nylon or polyester, must be worn.** Special fire-resistant lab coats are more expensive, but recommended for labs using these reagents routinely.

Please refer to the NJIT Chemical Hygiene Guide and Hazard Assessment Form to determine the proper PPE for handling corrosive materials.

☐ ☐ ☐ ☐ ☐ ☐ ☐

3. ENGINEERING/VENTILATION CONTROLS

- Many pyrophoric chemicals release noxious or flammable gases and should be handled in a laboratory chemical fume hood. In addition, some pyrophoric materials are stored under kerosene (or other flammable solvent), therefore the use of a fume hood (or glove box) is required to prevent the release of flammable vapors into the laboratory.
- Gloveboxes are an excellent device to control pyrophoric chemicals when inert or dry atmospheres are required.

Please review the NJIT Chemical Hygiene Guide and the Safe Chemical Fume Hood Use Guide for information on the proper use of a chemical fume hood and criteria for implementing engineering controls.

☐ Chemical Fume Hood ☐ Glovebox ☐ Biological Safety Cabinet ☐ Other _____

Room Location of Unit(s): _____

4. SPECIAL HANDLING PROCEDURES AND STORAGE REQUIREMENTS

- **Before** working with pyrophoric reagents, read the relevant Safety Data Sheets (SDS) and understand the hazards. The SDS must be reviewed before using an unfamiliar chemical and periodically as a reminder.

Pyrophorics users must be thoroughly-trained in proper lab technique and working alone with pyrophorics is strongly discouraged.

- Set up your work in a laboratory fume hood or glove box, and **ALWAYS** wear the appropriate personal protective equipment.
- Minimize the quantity of pyrophoric reagents used and stored.
- The use of smaller syringes is encouraged. If handling more than 20 ml of sample - one should use a cannula for transfer or use a 20 ml syringe repeatedly.

Storage

- Pyrophoric chemicals should be stored under an atmosphere of inert gas or under kerosene as appropriate.
- Avoid areas with heat/flames, oxidizers, and water sources.
- Containers carrying pyrophoric materials must be clearly labeled with the correct chemical name and hazard warning.
- For storage, prepare a storage vessel with a septum filled with an inert gas
    - Select a septum that fits snugly into the neck of the vessel
    - Dry any new empty containers thoroughly
    - Insert septum into neck in a way that prevents atmosphere from entering the clean dry (or reagent filled) flask.
    - Insert a needle to vent the flask and quickly inject inert gas through a second needle to maintain a blanket of dry inert gas above the reactive reagent.
    - Once the vessel is fully purged with inert gas, remove the vent needle then the gas line.

- For long-term storage, the septum should be secured with a copper wire (figure 4A).
- For extra protection, a second same-sized septa (sans holes) can be placed over the first (figure 4b).
- Use parafilm around the outer septa and (obviously) remove the parafilm and outer septa before accessing the reagent through the primary septa

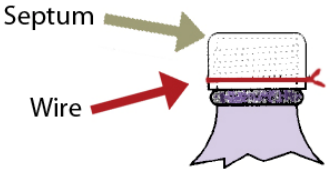

Fig. 4A Septa wired to vessel

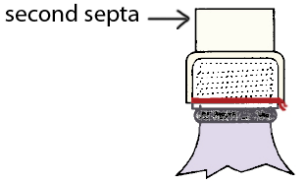

Fig. 4B For long-term storage, use a second septa

5. INCIDENTS AND ACCIDENTS

- Powdered lime should be used to completely smother and cover any spill that occurs.
- A container of powdered lime should be kept within arm's length when working *with a pyrophoric material.*
- *If anyone is exposed, or on fire, wash with copious amounts of water.*
- *The recommended fire extinguisher is a standard dry powder (ABC) type. Class D extinguishers are recommended for combustible solid metal fires (e.g, sodium,* LAH), but not for organolithium reagents.

Please review the SDS, verify with the manufacturer, or contact EHS for proper spill response. If it is safe to do so, prevent the spill from spreading be applying sand, earth or other non-combustible material. Contact NJIT Public Safety to activate emergency response personnel.

Laboratory personnel are to report all occupational injuries or illnesses to Faculty/PI as soon as practical. The Faculty/PI and laboratory personnel must submit the required paperwork to NJIT EHS Department. See the the Emergency Response Guidelines posted in the laboratory or Emergency Procedures section of the NJIT CHG for proper procedures involving an injury, exposure, fire, or release/spill of a hazardous material.

In the event of an emergency, DIAL 9-1-1 to activate emergency response personnel.

6. SPILL AND DECONTAMINATION

Wear proper PPE. Please review the SDS, verify with the manufacturer, or contact EHS for appropriate decontamination procedures. Dispose of all used contaminated disposables in the appropriate waste stream following the Waste Disposal Section of the NJIT CHG.

Decontamination Solution(s): _____

Additional Spill / Decontamination Requirements:

7. WASTE DISPOSAL

Follow the practices and procedures in accordance with the NJIT Laboratory Waste Management Program to properly dispose of waste. Unless the material is still in the original vendor's container, pyrophorics generally need to be "quenched" before giving to EHS for disposal.

Disposal of Pyrophoric Reagents

- A container with any residue of pyrophoric materials should never be left open to the atmosphere.
- Any unused or unwanted pyrophoric materials must be destroyed by transferring the materials to an appropriate reaction flask for hydrolysis and/or neutralization with adequate cooling.
- The essentially empty container should be rinsed three times with an inert dry solvent; this rinse solvent must also be neutralized or hydrolyzed.
- After the container is triple-rinsed, it should be left open in back of a hood or atmosphere at a safe location for at least a week. After the week, the container should then be rinsed 3 times again.

Disposal of Pyrophoric Contaminated Materials

- All materials that are contaminated with pyrophoric chemicals should be disposed of as hazardous waste.
- Alert the EHS Department for any wastes contaminated by pyrophoric chemicals.
- The contaminated waste should **not** be left overnight in the open laboratory, but **must** be properly contained to prevent fires.

Additional Waste Disposal Requirements:

8. PRIOR APPROVAL/REVIEW

9. DESIGNATED USE AREA

Designated Use Area Location(s): _____

10. SAFETY DATA SHEETS

Location of SDS: _____

11. LAB-SPECIFIC INFORMATION **(required)** ***(Examples of appropriate content)***

Appendix – List of Organolithium Reagents

Alkyls –

- Methyl-d3-lithium, as complex with lithium iodide solution 0.5 M in diethyl ether
- Methyllithium lithium bromide complex solution
- Methyllithium solution purum, ~5% in diethyl ether (~1.6M)
- Methyllithium solution purum, ~1 M in cumene/THF
- Methyllithium solution 3.0 M in diethoxymethane
- Methyllithium solution 1.6 M in diethyl ether
- Ethyllithium solution 0.5 M in benzene/cyclohexane (9:1)
- Isopropyllithium solution 0.7 M in pentane
- Butyllithium solution 2.0 M in cyclohexane
- Butyllithium solution purum, ~2.7 M in heptane
- Butyllithium solution 10.0 M in hexanes
- Butyllithium solution 2.5 M in hexanes
- Butyllithium solution 1.6 M in hexanes
- Butyllithium solution 2.0 M in pentane
- Butyllithium solution ~1.6 M in hexanes
- Butyllithium solution technical, ~2.5 M in toluene
- Isobutyllithium solution technical, ~16% in heptane (~1.7 M)
- sec-Butyllithium solution 1.4 M in cyclohexane
- tert-Butyllithium solution purum, 1.6-3.2 M in heptane

- tert-Butyllithium solution 1.7 M in pentane
- (Trimethylsilyl)methyllithium solution 1.0 M in pentane
- (Trimethylsilyl)methyllithium solution technical, ~1 M in pentane
- Hexyllithium solution 2.3 M in hexane
- 2-(Ethylhexyl)lithium solution 30-35 wt. % in heptane

Alkynyls –

- Lithium acetylide, ethylenediamine complex 90%
- Lithium acetylide, ethylenediamine complex 25 wt. % slurry in toluene
- Lithium (trimethylsilyl)acetylide solution 0.5 M in tetrahydrofuran
- Lithium phenylacetylide solution 1.0 M in tetrahydrofuran

Aryls –

- Phenyllithium solution 1.8 M in di-n-butyl ether

Others –

- 2-Thienyllithium solution 1.0 M in tetrahydrofuran
- Lithium tetramethylcyclopentadienide
- Lithium pentamethylcyclopentadienide