Section 5.29 Title: Using Pyrophoric Reagents **Revision Date:** 11/01/19
Prepared By: John F. Berry and Michael Roy **P.I.:** Prof. John F. Berry

Prior Approval: This procedure **IS** considered hazardous enough that prior approval is needed from the Principal Investigator.

Involves Use of Particularly Hazardous Substance (PHS)? No
___ Carcinogen ___ Reproductive Toxin ___ High Acute Toxicity
Does this procedure require medical surveillance? No
Does this require use of a fit-tested respirator? No

Brief Description of Procedure:
Use of pyrophoric solids or liquids.

Location: *List the locations (buildings/rooms) where this procedure may be performed. For use of a PHS indicate a more precise location within the room, if appropriate, as a designated area.*
Daniels Chemistry - All Berry group labs

Chemicals Involved:

Chemical	Physical or Health Hazard (e.g. carcinogen, corrosive)
See examples below	Pyrophoric; consult relevant SDSs for more details

Other Hazards: *Include hazards, other than chemical, that may be present during operation of the procedure.*
N/A

Exposure Controls: *(Check all that apply)*
PPE: _X_ Safety Glasses ___ Face Shield ___Chemical Splash Goggles
___Chemical Apron _X_ Gloves (Nitrile) _X_ Lab Coat
___Respirator (type) ___Other:
(Additional PPE may be warranted depending on the particular reaction.)

Engineering Controls:
_X_ Fume Hood ___Biosafety Cabinet _X_ Glove box
___ Vented gas cabinet _X_ Other: A blast shield may be used in some cases.

Administrative Controls: *List any specific work practices needed to perform this procedure (e.g., cannot be performed alone, must notify other staff members before beginning, etc.).*

All researchers must receive permission and training from Prof. Berry before handling pyrophorics. No lab member may work alone with pyrophoric substances. Notify other group members before working with pyrophoric materials.

Task Hazard Control Table: *For procedures involving numerous steps, it may be convenient to indicate specific requirements for individual tasks in the table below:*

N/A

Waste Disposal: *Describe any chemical waste generated and the disposal method used.*

Quench pyrophoric reagents immediately and appropriately. EH&S will accept original reagent bottles containing excess, unquenched pyrophorics.

Accidental Spills: *Describe the procedure for handling small chemical spills that may occur during this procedure. Note that for large spills it may be appropriate to call 911.*

Class-D (yellow) fire extinguishers should be used for metal fires.

Decontamination Procedures (required for PHS use): *Describe the procedure for decontamination of personnel and equipment.*

N/A

Training: *Describe any training needed prior to performing this procedure. Include training performed in-lab and any required demonstrations of competency.*

Formal training and documentation is required. Training is done on an individual basis by Prof. Berry.

Principle Investigator Approval: I have reviewed this procedure and approved it for use. Note: Modifications to the procedure may require update to this form.

Name: John F. Berry Signature: _____ Date: _____

Using Pyrophoric Reagents

Pyrophoric (py·ro·phor·ic; pī-rə-ˈfȯr-ik): igniting spontaneously

Pyrophoric chemicals are liquids, solids, and gases that will ignite spontaneously in air at or below 55 °C. Oxidation of the compound by oxygen or moisture in air proceeds so rapidly that ignition occurs. Many finely divided metals are pyrophoric, and their degree of reactivity depends on particle size, as well as factors such as the presence of moisture and the thermodynamics of metal oxide or metal nitride formation. Other reducing agents, such as metal hydrides, alloys of reactive metals, low-valent metal salts, and iron sulfides, are also pyrophoric. Appended at the end is a list of common pyrophoric compounds that are commonly used in inorganic synthesis.

General Considerations

Pyrophoric compounds are not to be used in the Berry lab without express consent from Prof. Berry. In most cases, training to use such substances will be done by Prof. Berry personally. This training must be documented. It is also good practice to discuss your procedure with other coworkers in the department who have relevant expertise.

Considerations for Storage of Pyrophoric Compounds

- Pyrophoric chemicals must be stored under an atmosphere of inert gas or under an appropriate liquid.
- Do not store pyrophoric chemicals with flammable materials or in a flammable-liquids storage cabinet.
- Store these materials away from sources of ignition.
- Minimize the quantities of pyrophoric chemicals stored in the laboratory.
- Store bottles of liquid pyrophorics inside the original metal shipping can, if available, to provide additional protection/secondary containment.
- Never return excess chemicals to the original container. Small amounts of impurities may be introduced into the container which may cause a fire or explosion.
- Date containers upon initial receipt and upon opening. Take note of any printed expiration dates on the container label and dispose of them as required. Many pyrophoric reagents become unstable or more dangerous with age.

Considerations for purchase of pyrophoric compounds

- Do not use pyrophoric chemicals if less-hazardous alternatives are possible.
- Purchase pyrophoric reagents in the minimum quantity required for the work to be performed. Initial cost per volume/weight may be lower when reagents are purchased in bulk, but repeated opening of containers and puncturing of septa leads to product degradation and loss. Wasted material and disposal cost will often offset any initial savings.
- Purchase the lowest concentration of pyrophoric chemicals that will meet your research needs.

Considerations for work space

- Work with pyrophoric chemicals in areas that you've designated especially for this work.

- Post a sign on the fume hood when a process involving pyrophoric chemicals is unattended.
- Remove all other chemicals and hazardous materials from the work area.
- Remove combustible materials from the work area.

Considerations for handling

- Do not handle pyrophoric chemicals when working alone.
- Notify other lab occupants when work with pyrophoric chemicals is in progress.
- Immediately close all containers of pyrophoric chemicals after use and return them to their designated storage location.

Considerations for PPE

- Consider the potential exposure and health consequences when selecting personal protective equipment (PPE) for tasks involving pyrophoric chemicals.
- Wear closed toed shoes made of a nonporous material; leather is preferred.
- In addition to the minimum lab apparel and PPE requirements, other protective equipment may be necessary to reduce risks. Additional equipment may include tight-fitting chemical splash goggles, a face shield, chemical-resistant gloves, or disposable lab coats. A blast shield may also be appropriate. Wear a cloth labcoat or apron that can be quickly removed if needed.
- Unless work will be performed in a glove box, it is highly recommended that a fire-resistant lab coat be worn while manipulating quantities of liquid pyrophorics over 10 mL or solid pyrophorics over 1 gram.
- Disposable nitrile gloves provide adequate protection against accidental hand contact with small quantities of most laboratory chemicals, but are highly combustible. Consider the use of Nomex/Leather pilot's gloves, which provide fire resistance without compromising manual dexterity. The pilots gloves should be worn over nitrile gloves and are recommended during syringe/cannula transfers of pyrophoric liquids.
- Contact EHS for general assistance with risk assessments, glove compatibility, and other PPE selection.

Considerations for waste and decontamination

- Pyrophorics that remain after setting up an experiment should be quenched and disposed of promptly. Beware of bringing paper trash contaminated with pyrophorics out of the glove box.
- Decontaminate all surfaces that have come in contact with pyrophoric chemicals and clean-up small spills promptly.
- EHS will accept reagent bottles containing unquenched pyrophorics.

Considerations for an emergency

- If there is fire on your clothing or skin, stop-drop-and roll, unless you are within a few feet of a safety shower.
- Keep in mind that unreacted materials may reignite until they are washed off.
- If you are contaminated with a pyrophoric, remove your contaminated clothing while using the safety shower. The copious amounts of water will flush away the heat of reaction.

- If you have significant amounts of dry reactive compound on your body, you may brush off the bulk of it before you enter the shower, however only if it is not reacting.
- Contain any spill and/or extinguish the fire only if you can do so safely.
- If you cannot contain the spill, evacuate the lab and contact 911 and EHS immediately.
- A MetL-X fire extinguisher is available near the elivators. CO_2 extinguishers can cause some pyrophorics to react more vigorously. Powdered lime can be used to cover spills and slow the reaction with air/humidity.

References

Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards (section *4.D.2.2 Pyrophorics*) The National Academies Press: Washington, DC, 2011.
https://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Aldrich/Bulletin/al_techbull_al134.pdf
https://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Aldrich/Bulletin/al_techbull_al164.pdf

Appendix: Common Pyrophoric Reagents

Solids

- White phosphorus
- Alkali metals (lithium, sodium, potassium, rubidium, caesium), including the alloy NaK
- Finely divided metals (iron, aluminium, magnesium)
- Potassium graphite (KC_8)
- Metal hydrides (sodium hydride, lithium aluminium hydride)
- Methane tellurol (CH_3TeH)
- Partially or fully alkylated derivatives of metal and nonmetal hydrides (diethylaluminium hydride, trimethylaluminium, triethylaluminium, butyllithium), with a few exceptions (i.e. dimethylmercury and tetraethyllead)
- Grignard reagents (compounds of the form RMgX)
- Used hydrogenation catalysts such as palladium on carbon or Raney nickel (especially hazardous because of the adsorbed hydrogen)

Liquids

- *tert*-Butyllithium
- Solutions of methyllithium, butyllithium
- Diethylzinc
- Triethylaluminium

Hydrazine is hypergolic with oxidants like dinitrogen tetroxide or hydrogen peroxide, but not truly pyrophoric.

Gases

- Nonmetal hydrides (arsine, phosphine, diborane, germane, silane)