|  |  |
| --- | --- |
| **Brueckner Lab-Specific Standard Operating Procedure (LSOP) Metal Hydrides for Reductions** | |
| **Principal Investigator(PI):** Christian Brückner | |
| **Building:** Chemistry | **Lab(s) Covered by LSOP:** R413/R415 |
| **Department:** Chemistry | **Lab Phone Number(s):** 6-6596/6-6598 |
| **SECTION 1 – HAZARDOUS CHEMICAL(S) or PROCESS(ES) and HAZARDS INVOLVED** | |
| 1. Di-isobutyl Aluminum Hydride (DIBAL-H) (typically as 1M solution in hexane in SureSeal®bottles) 2. Lithium Aluminum Hydride (LAH) (typically a grey solid) 3. Sodium Borohydride (NaBH4) (typically a white solid)  * Flammable – particularly when in organic solutions * Corrosive. Skin corrosion/burns. May cause ocular damage. * Respiratory Sensitization. Material may be carcinogenic and cause reproductive toxicity. Target organ exposure from repeated exposures. * Severe Toxicity. May cause severe injury or death | |
| **SECTION 2 – ADMINISTRATIVE CONTROLS** | |
| * Lab-specific safety training must be provided by the principal investigator (PI) or other qualified personnel to all researchers working with ozone. Documentation of training is required. * Read the safety data sheet (SDS) for the specific material prior to use: <http://www.msds.com> (search for ozone in oxygen) * Researchers must not work alone with ozone. * Experiments should be performed during normal business hours (i.e., 8:00 am-5:00 pm Mon-Fri), if possible. * Whenever possible, find safer substitutes or carry out reductions in smaller quantities * An eyewash and safety shower must be in the immediate work area | |
| **SECTION 3- ENGINEERING CONTROLS** | |
| * All work with chromium reagents must be conducted in a chemical fume hood, under dry conditions, with the sash at the lowest working height and with sliding sash panels (if applicable) aligned to form a barrier between the researcher and the experiment. * Chemical fume hoods must have been tested by EHS within the last year. If the hood is not working properly, contact Facilities (486-3113) to repair the hood or EHS to retest (486-3613). | |
| **SECTION 4 – WORK PRACTICES** | |
| * Since compounds like DIBAL-H are stored in the fridge (R413), allow to warm to room temperature before using. Wipe off any water around the bottle using a dry paper towel. * Make sure that there are no other flammable materials such as other solvents, chemicals or paper in the fume hood. * Always make sure that the syringe and needle you use to take out the chemical are dry and that the syringe was flushed with nitrogen several times immediately prior to use * 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. * 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. Any residue in the syringe or needle used should also be quenched in this manner. * Remove the balloon-needle from the bottle as soon as possible after the transfer and re-cap and seal the bottle with Parafilm before replacing in the refrigerator as described above. * In the case for LAH and NaBH4, they are stored in desiccators * Weighing should be carried out fast and ensure there are no spills on the balance. | |
| **SECTION 5 – PERSONAL PROTECTIVE EQUIPMENT (PPE)** | |
| * At a minimum, a lab coat, closed-toed footwear and chemical safety splash goggles that meet ANSI standard Z-87.1 must be worn. * Nitrile gloves indicated in the safety data sheet (SDS) must be worn and no skin should be exposed. * Full-face shield should be used if the experiment is being conducted on a larger scale i.e., exceeding 25 ml of hydride solution of 5 g of solid material. | |
| **SECTION 6 – STORAGE** | |
| * All containers must be clearly labeled with the chemical name and hazard classes and kept tightly-sealed. * Ensure labels on original bottles remain legible and prominently displayed to identify contents. * Store compounds away from oxidizing agents and in a cool, dry environment, preferably in the fridge for DIBAL-H and desiccators for NaBH4 and LAH. | |
| **SECTION 7 – SPILL AND ACCIDENT PROCEDURES** | |
| * Evacuate the laboratory * Close door(s) to lab and post a “**NO ENTRY**” sign(s) or other warning information on the door, detailing the type of hazard inside * Activate the fire alarm and call 911, detailing the type of emergency * Do not re-enter area until instructed to do so by UCFD or other emergency personnel. Report accident to Dr. Brückner and EH&S. | |
| **SECTION 8 – FIRST AID PROCEDURES** | |
| |  |  | | --- | --- | | First Aid- Eyes | 1. Immediately move to the eyewash station, hold eyelids open and flush with water. Remove contact lenses while flushing (if applicable). 2. Have another person from the lab dial 911and specifically mention compound exposure. 3. Continue flushing the eyes until emergency personnel arrives. | | First Aid- Skin | 1. Immediately move to safety shower or other water source and begin rinsing affected area(s). Remove contaminated clothing (if applicable) while flushing. 2. Have another person from the lab dial 911and specifically mention exposure. 3. Flush affected area(s) under safety shower for at least 15 minutes. 4. Keep applying ointment or rinsing affected area(s) until emergency personnel arrives. | | First Aid- Ingestion | 1. Immediately rinse the mouth with cold water. Do NOT induce vomiting. Do NOT give emetics or baking soda. 2. Have another person from the lab dial 911 and specifically mention exposure. | | First Aid- Inhalation | 1. Move to fresh air. 2. Dial **911.** 3. Inform emergency responders of accident involved. | | |
| **SECTION 9 – WASTE MANAGEMENT** | |
| * All waste should be disposed of after carful quenching using isopropanol under the fume hood. Allow the quenching reaction to come to completion (no further gas evolves). * Disposable syringes and needles need to disposed in the appropriate waste/sharps container after rinsing with isopropanol. * All quenched chemical waste must be labeled with “Hazardous Waste” stickers or tags, use full chemical names to describe the waste, be stored in sturdy, plastic containers with tight-fitting caps or lids, and be stored alone or with other compatible chemicals. * Hazardous wastes must be stored at or near a green “Satellite Accumulation Area” sign prior to disposal by EH&S. Once the containers are 80% filled, fill our EH&S chemical waste pickup form: [esh.uconn.edu/Regulated%20Waste%20Management/index.php](http://ehs.uconn.edu/Regulated%20Waste%20Management/index.php) * The [Chemical Waste Disposal Manual](http://ehs.uconn.edu/Chemical/ChemWasteDisp.pdf) must be used as a reference | |
| **SECTION 10 – DECONTAMINATION PROCEDURES** | |
| Work Area:   * Collect all of the hydride in a suitable and carefully and completely quenched the hydride with isopropanol. Dispose in the appropriate waste container * Glassware should be cleaned within a few seconds of use * Removal - Equipment can be decontaminated through a water rinse using a pressurized or gravity flow * Solidifying liquid or gel contaminants to enhance physical removal | |
| **SECTION 11 – SPECIFIC PROCEDURE** | |
| A typical use of DIBAL-H can be found in: Brückner, C.; Ogikubo, J.; McCarthy, J. R.; Akhigbe, J.; Hyland, M. A.; Daddario, P.; Worlinsky, J. L.; Zeller, M.; Engle, J. T.; Ziegler, C. J.; Ranaghan, M. J.; Sandberg, M. N.; Birge, R. R., meso-Arylporpholactones and their Reduction Products. *J. Org. Chem.* **2012,** *77* (15), 6480-6494.  ***General Procedure for the Preparation of Hemiacetals by DIBAl-H Reduction of Lactones***  [*meso-*Tetraphenylporpholactonato]Zn complex (1.4 × 10−4 mol, ∼95 mg) were dissolved under an atmosphere of N2 in dry THF (20−25 mL) and cooled to −78 °C. To it was added 20% DIBAl-H (1.0 mL of a 20 wt % solution in hexane, ∼7.0 equiv). The reaction mixture stirred for 60 min at this temperature and then allowed to warm to ambient temperature. A noticeable color change from green to blue took place during this time. Once warm, the reaction was quenched by addition of a few drops of water. The solution was then transferred to a separatory funnel, diluted with CH2Cl2 (∼25 mL), washed twice with 0.1 M aq. HCl, and once with H2O. The organic layer was collected and dried over anhydrous MgSO4. The solution was then evaporated to dryness by rotary evaporation and used as is or purified by preparative plate or column chromatography.  A typical use of LAH can be found in: Brückner, C.; Xie, L. Y.; Dolphin, D. ‘The Reductive Coupling of 2-Cyanopyrroles: A Study Pertaining to the Mechanism of Formation of Porphocyanines’ *Tetrahedron* **1998**, *54*, 2021–2030.  ***Bis(2-pyrrolylmethyl)amine***  (2-Pyrrolylmethene)-(2-pyrrolylmethyl)imine (0.10 g, 0.58 mmol) dissolved in THF (10 mL) was added under anhydrous conditions and at 0°C to a suspension of LAH (44 mg, 2 equiv.) in dry THF (5 mL). The reaction mixture was quenched with Glauber’s salt (Na2SO4.10 H2O, ca. 0.2 g) and the resulting slurry filtered through a pad of Celite®. The filtrate was evaporated on a rotary evaporator to give the desired amine as a colorless and odorless oil.  A typical use of NaBH4 can be found in: Briñas R. P.; Brückner, C. ‘Synthesis of 5,10-Diphenylporphyrin’ *Tetrahedron* **2002**, *58*, 4375–4381.  ***5,10-Diphenylporphyrin***  To a stirred solution of diacyl dipyrromethane (50 mg, 0.14 mmol) in THF/methanol (10:1, 6 mL) was added, under N2, NaBH4 (0.11 g, 2.8 mmol) in small portions (~every 2 mins). After 40 mins at r.t, the reaction mixture was poured into a mixture of saturated aq NH4Cl and CHCl3 (1:1, 20 mL). The organic phase was isolated, washed with water (2x) and dried (Na2CO3). The solvent was evaporated under vacuum. | |

|  |  |  |  |
| --- | --- | --- | --- |
| **SECTION 12A. APPROVAL** | | | |
| I have reviewed, understand and agree to follow this lab-specific standard operating procedure (LSOP)*.* Failure to follow this LSOP or lab-specific training guidelines is a violation of the [*University Health & Safety Policy*](http://policy.uconn.edu/2011/05/19/health-and-safety-policy/) and [*University Code of Conduct*](http://policy.uconn.edu/2011/05/17/employee-code-of-conduct/).  Further approval and/or review of this LSOP by Dr. Brückner is required if any of the following events occur:   * A significant change in amount (i.e., doubling of the scale of reaction) or substitution of the chemicals in the procedure is planned * A major change in the agreed-upon experimental set-up is planned (heating instead of room temp, etc.) * Any signs of a failure in safety design or equipment are observed * Any signs or symptoms of a chemical exposure to any personnel are observed * Unexpected and/or potentially dangerous experimental results occur (e.g., fire, uncontrolled buildup of heat and/or pressure, etc.) | | | |
| **Researcher Name/Signature** | **Trainer Name/Signature** | **Training Date** | |
|  |  |  | |
|  |  |  | |
|  |  |  | |
|  |  |  | |
|  |  |  | |
|  |  |  | |
|  |  |  | |
|  |  |  | |
| **SECTION 12B. PRINCIPAL INVESTIGATOR CERTIFICATION** | | | |
| I approve the contents of the lab-specific standard operating procedure listed above. | | | |
| **PI Signature:** | | | **Date:** |
| **A HARD OR ELECTRONIC COPY (https://bruckner.research.uconn.edu/safety-resources/) OF EACH LAB-SPECIFIC STANDARD OPERATING PROCEDURE MUST BE READILY AVAILBALE IN THE LAB.** | | | |