

SOP for the Titration of alkylolithiums

prepared by Dr. John Trant, February 1st, 2013.

When to titrate: If it has been seven days since the last titration or if more than 20 % of the bottle has been removed since the last titration. Please seek assistance if you are not familiar with handling alkylolithiums. They are very, very dangerous.

- 1) Using the approximate nominal concentration on the bottle (x), add approximately (x/2) mmol of diphenylacetic acid to a flame dried round-bottomed flask equipped with a stir bar under inert atmosphere (25 mL flask)—do this in triplicate noting the mass of diphenyl acetic acid exactly!
- 2) Add freshly distilled (DRY!!!!) THF to the flasks under argon (~ 10 mL)
- 3) Titration should require around 500 microlitres of alkyl lithium. Use a glass, gastight syringe (WARNING: BuLi can cause extreme burns and autoignites on contact with air, other alkylolithiums are even more sensitive. If unfamiliar with the reagent, please, please, please ask someone for assistance and/or training). Transfer 400 microlitres, relatively rapidly, to a flask with stirring.
- 4) The diphenyl acetate anion is yellow. Precipitate will form during the titration, this is normal and NOT indicative of the endpoint.
- 5) Add the remaining (in excess of the 400 uL) BuLi slowly and dropwise until a yellow colour persists, record the volume added.
- 6) Repeat the titration with the other two flasks and calculate the concentration of BuLi (mmol diphenyl acetic acid/ volume (mL) of BuLi added).
- 7) If all three measurements agree within 0.05 M of the average (or close enough) record the concentration, initials, and date on the bottle. If the concentration agreement is not satisfactory, repeat the titration until three calculations agree.
- 8) Quench syringe carefully in isopropanol and wash the syringe with 10 % HCl, water, acetone, and DCM.
- 9) Quench the titration flasks with water and discard as aqueous waste.
- 10) Ensure the sure-seal on the alkyl lithium is reasonably intact. Cover with Teflon tape if significant puncture damage is evident. Seal the flask and wrap the joint of lid and bottle with parafilm to reduce air exchange.

To quench an empty (or no longer useful) bottle: Cool the bottle in an ice bath. Under an inert gas atmosphere, dilute with dry THF or hexanes. Quench with dropwise addition of isopropanol until reaction stops (no significant heat is generated). Carefully remove the sure seal, and, at 0 °C, add water until no more reaction is observed. Finish the quench with ammonium chloride solution, and discard the mixture as aqueous waste.