

Handout: Borane

Preparation of tert-Butylamine borane, $t\text{-BuNH}_2\text{BH}_3$

- 1) **In a hood:** to a mixture of solid sodium borohydride (**1.0 g**, 0.026 mol) and ammonium chloride (**0.71 g**, 0.013 mol) in **125 mL** Erlenmeyer flask add toluene (**15 mL**) and t-butylamine (**2.5 mL**, 0.025 mol).
- 2) While stirring, add water (**2 mL**).
- 3) Continue stirring until slightly exothermic reaction slows down and fast gas evolution ceased after ~10 min (CAUTION: hydrogen gas! Flammable!). Temperature rises spontaneously to ~35 °C, then drops.
- 4) Heat the reaction mixture in flask for 10 min on nearly boiling water bath to evaporate ammonia and an excess of t-butylamine, then remove flask from water bath. Cover neck of the flask with aluminum foil and bring the flask to your bench.
- 5) Add drying agent, sodium sulfate (2.5 g). Shake reaction mixture and let to stay for 5 min.
- 6) Decant solution carefully into another 125mL Erlenmeyer flask. Rinse solid in reaction flask with toluene (**10 mL**). Decant.
- 7) To the combined toluene solutions, add petroleum ether (**100 mL**). Complete precipitation of the product at 0 °C, using ice-water bath (~10 min).
- 8) Vacuum filter crystals of tert-butylamine borane. Weight. Calculate %yield.
- 9) Measure m.p. and take IR-spectrum. Weight 20 mg in disposable NMR-tube for further ^1H NMR analysis (**sample 0**).

Preparation of tert-Butylamine iodoborane, $t\text{-BuNH}_2\text{BH}_2\text{I}$

- 1) **In a hood:** to a mixture of t-butylamine borane (**0.70 g**, 0.008 mol) and toluene (**3 mL**) in a Schlenk tube **under the stream of dry nitrogen**, add solid iodine (**1.0 g**, 0.004 mol), carefully, portionwise, until slightly brown solution (Exothermic reaction! Hydrogen gas evolution! HI fumes!). To the solution, add small amount of t-butylamine borane, until colorless. Cap the tube with septum. Bring it to your bench.
- 2) Weight disposable NMR-tube. Using Pasteur pipet, transfer 0.2-0.3 mL of iodoborane solution into NMR tube (Careful: fuming in the air!). Recap the Schlenk tube.
- 3) In NMR-tube, precipitate the product by adding petroleum ether to the top of NMR-tube. Cap and shake NMR-tube. Let the solid to settle. Decant solution. Make a hole in a cap for NMR-tube. Cap the tube using cap with hole and vacuum the tube until no longer cold, using house vacuum line.
- 4) Weight NMR tube, cap it with normal cap and save for further ^1H NMR-analysis (**sample 1**).

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Should be done the same day as preparation of unstable tert-Butylamine iodoborane $t\text{-BuNH}_2\text{BH}_2\text{I}$.

Preparation of boronium cation, di-(tert-butylamine)boronium iodide, $[t\text{-BuNH}_2\text{BH}_2\text{NH}_2\text{Bu-t}] \text{I}$

- 1) Bring **in a hood** remaining tert-butylamine iodoborane solution in Schlenk tube.
- 2) Using a pipet, carefully add an excess of t-butylamine (**1 mL**), until no more precipitate formed (CAUTION: exothermic reaction! Vapors of toxic amine!)
- 3) Take off (decant) mother liquor from the Schlenk tube. Rinse the solid with toluene: add toluene (**3 mL**) to the solid, cap the tube, shake it, open and take off solution (decant or use Pasteur pipet).
- 4) Vacuum Schlenk tube with the product using manifold, until the constant weight. Calculate %yield from t-butylamine borane.
- 5) Measure m.p. Take IR of the solid. Weight 20 mg in NMR-tube for further ^1H NMR-analysis (**sample 2**).

Exchange of amine part in your amine boronium iodide prepared

- 1) **In a hood**: Dissolve 20 mg of amine boronium iodide prepared in other amine provided. Use Schlenk tube. Carefully evaporate amine into manifold. Repeat 2 times with fresh amine. Do not use more than 3-5 mL each time. Collect solid, weight it, measure m.p. and put 5 mg in NMR tube provided (**sample 3**).

Preparation of t-butylamine borane, $t\text{-BuNH}_2\text{BH}_3$ from boronium cation, di-(tert-butylamine)boronium iodide and sodium borohydride

- 1) In 125 mL Erlenmeyer flask weight boronium cation iodide (**0.56 g**, 0.0020 mol) and sodium borohydride (**0.16 g**, 0.0040 mol).
- 2) **In a hood**, add to the mixture toluene (**10 mL**) and then water (**1 mL**). Stir until no more gas evolves (~ 20 min).
- 3) Decant solution carefully to another 125 mL E. flask. Dilute with petroleum ether (100 mL). Let stay at 0 °C for complete precipitation.
- 4) Vacuum filter the product. Weight and calculate % yield based on boronium cation. Measure m.p. and IR to compare with the same taken for above sample.
- 5) Homework: assign the IR bands for borane and boronium cation. Assign ^1H NMR signals for borane, iodoborane and boronium cations, using integration pattern. Consult www.sigmaaldrich.com to download NMR-spectrum of t-butylamine and other amine used