

## **Buttressing Effects on Haloarene Deprotonation: A Merely Kinetic or also Thermodynamic Phenomenon?**

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### **Supporting Information**

Laboratory routine and abbreviations have been specified in previous publications.<sup>1 – 3</sup> <sup>1</sup>H and (<sup>1</sup>H decoupled) <sup>13</sup>C NMR were recorded at 400 and 101 MHz, respectively, the solvent being deuteriochloroform. The X-ray crystallographic data have been deposited with the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK, from where they can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html).

#### *Working Procedure:*

At -100 °C, biphenyl (approx. 0.3 g, 2 mmol), as an internal reference (“standard”) for gas chromatography quantification, (2,6-dichloro-4-iodophenyl)triethylsilane <sup>4</sup> (1.9 g, 5.0 mmol) and, 15 min later, (2,6-dichloro-3-iodophenyl)triethylsilane were added consecutively to a solution of *tert*-butyllithium (10 mmol) in tetrahydrofuran (25 mL) and pentanes (7 mL). Aliquots (of approx. 2.0 mL) were withdrawn after 3, 15, 45, 180 and 360 min to be poured into a solution of elemental bromine (approx. 0.05 mL, 1 mmol) in hexanes (3 mL). The organic phase was washed with a saturated aqueous solution (1.0 mL) of sodium sulfite before being subjected to gas chromatographic analysis (30 m, methylpolysiloxane DB-1, 180 °C; 30 m, polyethylene DB-WAX, 180 °C). The amounts of iodo and bromo compounds <sup>5, 6</sup> were calculated from the product/standard ratios and corrected using separately determined calibration factors.

**(2,6-Dichloro-4-iodophenyl)triethylsilane:** (2,6-Dichlorophenyl)triethylsilane (22 mL, 26 g, 0.10 mol) was added to a solution of *sec*-butyllithium (0.10 mol) in cyclohexane (80 mL) and tetrahydrofuran (0.12 L) kept in a dry ice bath. After 45 min at -75 °C, the reaction mixture was poured into a solution of elemental iodine (25 g, 0.10 mol) in tetrahydrofuran (0.10 L) at -75 °C. The reaction mixture was washed with a saturated aqueous solution (3 x 25 mL) of sodium sulfite. Upon distillation, a colorless oil was collected; b.p. 118 – 120 °C/0.2 mmHg;  $n_D^{20} = 1.5962$ ;  $d_4^{20} = 1.429$ ; yield: 21.3 g (55 %);  $^1\text{H}$  NMR: 7.60 (s, 2 H), 1.1 (m, 6 H), 1.0 (m, 9 H). –  $^{13}\text{C}$  NMR: 142.5, 136.8, 134.7, 94.6, 7.8 (3 C), 6.0 (3 C). –  $\text{C}_{12}\text{H}_{17}\text{Cl}_2\text{ISi}$  (387.15): calcd. C 37.22, H 4.43; found C 37.44, H 4.30.

**(2,6-Dichloro-3-iodophenyl)triethylsilane:** Diisopropylamine (14 mL, 10 g, 0.10 mol) and 1-iodo-2,4-dichlorobenzene (13 mL, 27 g, 0.10 mol) were added consecutively to a solution of butyllithium (0.10 mol) in hexanes (65 mL) and tetrahydrofuran (0.15 L) cooled in a dry ice/methanol bath. After 2 h at -75 °C, the mixture was treated with chlorotriethylsilane (18 mL, 16 g, 0.10 mol). Direct distillation afforded a colorless oil; b.p. 121 – 123 °C/0.3 mmHg;  $n_D^{20} = 1.5954$ ;  $d_4^{20} = 1.440$ ; yield: 32.5 g (84 %). –  $^1\text{H}$  NMR: 7.75 (d,  $J = 8.5$  Hz, 1 H), 6.93 (d,  $J = 8.5$  Hz, 1 H), 1.1 (m, 6 H), 1.0 (m, 9 H). –  $^{13}\text{C}$  NMR: 145.0, 142.3, 141.3, 137.1, 129.8, 98.9, 7.9 (3 C), 6.3 (3 C). –  $\text{C}_{12}\text{H}_{17}\text{Cl}_2\text{ISi}$  (387.15): calcd. C 37.23, H 4.43; found C 37.31, H 4.36.

**(3-Bromo-2,6-dichlorophenyl)triethylsilane:** Prepared as described in the preceding paragraph, from 1-bromo-2,4-dichlorobenzene (23 g, 0.10 mol); colorless oil; b.p. 115 – 117 °C/0.6 mmHg;  $n_D^{20} = 1.5660$ ;  $d_4^{20} = 1.325$ ; yield: 29.6 g (87%). –  $^1\text{H}$  NMR: 7.51 (d,  $J = 8.5$  Hz, 1 H), 7.09 (d,  $J = 8.5$  Hz, 1 H), 1.1 (m, 6 H), 1.0 (m, 9 H). –  $^{13}\text{C}$  NMR: 141.6, 138.4, 135.2, 130.2, 129.1, 123.2, 8.3 (3 C), 6.8 (3 C).  $\text{C}_{12}\text{H}_{17}\text{BrCl}_2\text{Si}$  (340.15): calcd. C 42.37, H 5.04; found C 42.36, H 5.16.

## References

- [1] Bobbio, C.; Schlosser, M.; *Eur. J. Org. Chem.* **2001**, 4533 – 4536.
- [2] Schlosser, M.; Heiss, C.; *Eur. J. Org. Chem.* **2003**, 4618 – 4624.
- [3] Schlosser, M.; Marull, M.; *Eur. J. Org. Chem.* **2003**, 1569 – 1575.
- [4] Prepared from the commercial 2,4-dichloro-iodobenzene and 1,3-dichloro-5-iodobenzene by simultaneous treatment with lithium 2,2,6,6-tetramethylpiperidide (LITMP) and chlorotriethylsilane in tetrahydrofuran at -75 °C ("*in situ* trapping") followed by immediate distillation.
- [5] Prepared from the commercial 1-bromo-2,4-dichlorobenzene and 1-bromo-3,5-dichlorobenzene, respectively, as described in the preceding footnote for the (2,6-dichloro-3- and -4-iodophenyl)triethylsilanes.
- [6] C. Heiss, E. Marzi, M. Schlosser, *Eur. J. Org. Chem.* **2003**, 4625 - 4629.