$(Bu_3Sn)_2$-TBAF: A New Combination Reagent for the Reduction and Deuteration of Aryl Bromides and Iodides.

Electronic Supplementary Information

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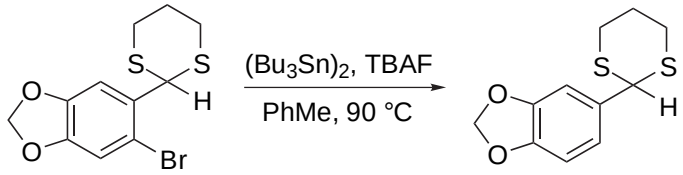
REPRESENTATIVE PROCEDURES

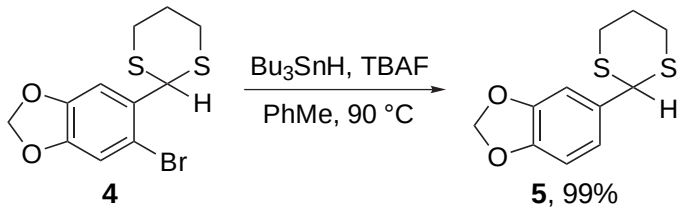
Reduction using $(Bu_3Sn)_2$-TBAF



4 **5**, 97%

5-Bromo-6-[1,3]dithian-2-ylbenzo[1,3]dioxole (**4**)[1] (80 mg, 0.25 mmol), hexabutylditin (189 μL, 0.375 mmol) and TBAF (1M soln. in THF:H_2O (95:5), 1.0 mL, 1.00 mmol) were heated in toluene (5 mL) at 90 °C for 1 h. The resulting solution was cooled to room temperature, solvents were removed *in vacuo* and the crude product was purified by flash column chromatography (10% KF/SiO_2, DCM) to yield 5-[1,3]dithian-2-ylbenzo[1,3]dioxole (**5**) as a white crystalline solid (58 mg, 0.24 mmol, 97%); m.p. 88 - 90°C (EtOH / water) lit.[2] 87 - 88°C (AcOH); ν_{max} (film) 2895 w, 1501 s, 1488 s, 1441 m, 1249 s, 1037 s cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.99 (1H, d, *J* 1.8 Hz, C<u>H</u>), 6.94 (1H, dd, *J* 8.1, 1.8 Hz, C<u>H</u>), 6.76 (1H, d, *J* 8.1 Hz, C<u>H</u>), 5.96 (2H, s, OC<u>H</u>$_2$O), 5.10 (1H, s, SC<u>H</u>S), 3.05 (2H, ddd, *J* 14.3, 12.1, 2.4 Hz, 2 x SC<u>H</u>H), 2.91 (2H, ddd, *J* 14.3, 4.4, 3.2 Hz, 2 x SCH<u>H</u>), 2.17 (1H, dtt, *J* 14.1, 4.4, 2.4 Hz, $SCH_2C\underline{H}HCH_2S$), 1.90 (1H, dtt, *J* 14.1, 12.1, 3.2 Hz, $SCH_2CH\underline{H}CH_2S$); δ_C (75 MHz, $CDCl_3$) 147.9 (<u>C</u>), 147.8 (<u>C</u>), 133.1 (<u>C</u>), 121.4 (<u>C</u>H), 108.5 (2 x <u>C</u>H), 101.4 (O<u>C</u>H_2O), 51.3 (S<u>C</u>HS), 32.3 (2 x S<u>C</u>H_2), 25.2 (<u>C</u>H_2); $^m/_z$ (EI) 240 (M^+, 52), 166 (100).

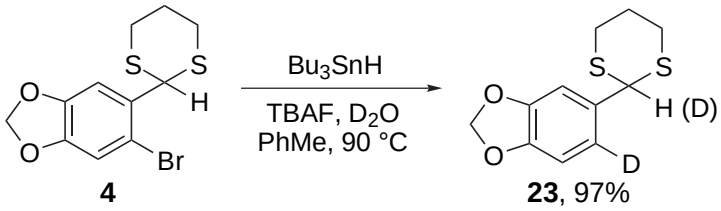
Reduction using Bu_3SnH-TBAF



4 **5**, 99%

5-Bromo-6-[1,3]dithian-2-ylbenzo[1,3]dioxole (**4**) (80 mg, 0.25 mmol), tributyltin hydride (134 μL, 0.50 mmol) and TBAF (1M soln. in THF:H_2O (95:5), 1.0 mL, 1.00 mmol) were heated in toluene (5 mL) at 90 °C for 1 h. The resulting solution was cooled to room temperature, solvents were removed *in vacuo* and the crude product was purified by flash column chromatography (10% KF/SiO_2, DCM) to yield 5-[1,3]dithian-2-ylbenzo[1,3]dioxole (**5**) as a white crystalline solid (59 mg, 0.25 mmol, 99%). Data as stated above.

Deuteration using $(Bu_3Sn)_2$-TBAF, D_2O



4 **23**, 97%

5-Bromo-6-[1,3]dithian-2-ylbenzo[1,3]dioxole (**4**) (80 mg, 0.25 mmol), hexabutylditin (189 μL, 0.375 mmol) and TBAF (1M soln. in THF:D_2O (95:5), 1.0 mL, 1.00 mmol) were heated in toluene (5 mL) at 90 °C for 1 h. The resulting solution was cooled to room temperature, solvents were removed *in vacuo* and the crude product was purified by flash column chromatography (10% KF/SiO_2, DCM) to yield the title compound (**23**) as a white crystalline solid (58 mg, 0.24 mmol, 97%); m.p. 81 - 84°C (ether/petrol); ν_{max} (film) 2892 w, 1477 s, 1420 w, 1274 w, 1240 m, 1039 m cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.99 (1H, s, C<u>H</u>), 6.76 (1H, s, C<u>H</u>), 5.96 (2H, s, OC<u>H</u>$_2$O), 5.10 (~0.5H, s, SC<u>H</u>S), 3.05 (2H, ddd, *J* 14.3, 12.1, 2.4 Hz, 2 x SC<u>H</u>H), 2.91 (2H, ddd, *J* 14.3, 4.4, 3.2 Hz, 2 x SCH<u>H</u>), 2.17 (1H, dtt, *J* 14.1, 4.4, 2.4 Hz, $SCH_2C\underline{H}HCH_2S$), 1.91 (1H, dtt, *J* 14.1, 12.1, 3.2 Hz, $SCH_2CH\underline{H}CH_2S$); δ_C (75 MHz, $CDCl_3$) 147.9 (<u>C</u>), 147.8 (<u>C</u>), 132.9 (<u>C</u>), 121.4 (<u>C</u>D), 108.5 (<u>C</u>H), 108.4 (<u>C</u>H), 101.4 (O<u>C</u>H_2O), 51.3 (S<u>C</u>HS), 32.3 (2 x S<u>C</u>H_2), 25.2 (<u>C</u>H_2); $^m/_z$ (EI): 241 (M^+, 100).

Footnote

Reactions have been realised in THF, DMF and 1,4-dioxane. They may be conducted at lower temperature but take appreciably longer. At RT, for example, reactions near completion after *ca.* 2 days.

References

1 D. C. Harrowven, *Tetrahedron*, 1993, **49**, 9039.

2 M. D. Rozwadowska and M. Chrzanowska, *Tetrahedron*, 1985, **41**, 2885.