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Ultrasound in Organic Synthesis. Electron-transfer Catalysis in Li-TMSCl Reductive Benzene Silylation and TMSCl Wurtz Coupling

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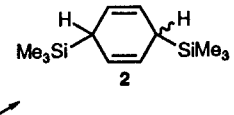
Di-*tert*-butylbiphenyl **1** and hexamethylphosphoric triamide (HMPT) are efficient catalysts for reductive benzene silylation or hexamethyldisilane **3** formation, respectively.

Existing reductive benzene silylation procedures result in unsatisfactory yields and require finely-dispersed lithium and prolonged stirring of reagents.[1] A concurrent reaction – Wurtz coupling of TMSCl to **3** – also contributes to diminishing the yields of 1,4-TMS derivatives of 1,4-dihydrobenzene **2**. In this communication it is shown that using ultrasound activation of Li and electron transfer catalyst **1** sufficiently decreases reaction times and suppresses the formation of **3**.



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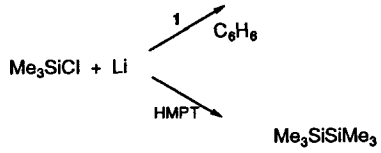
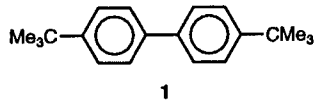


3



1

Interestingly, if benzene is omitted from the reaction mixture **1** does not catalyse TMSCl coupling to **3**. When **3** is required as a main product another electron-transfer reagent, HMPT, is found to be the catalyst of choice in THF solution with metallic Li-TMSCl. From this observation it may be deduced that a catalyst's ability to solubilise lithium is not sufficient for the particular reaction to proceed. Therefore, the compatibility of an electron transfer reagent and the particular reaction is a prerequisite. Thus, the efficiency of **1** is obviously associated with the ability of biphenyls to accept electrons and to pass them on to benzene. After this electron transfer follows silylation of benzene radical-anions in solution. Obviously, this electron transfer is sufficiently fast to prevent silylative deactivation of **1**. Inefficiency of **1** for Wurtz coupling of TMSCl is probably connected with the surface nature of this reaction or the catalyst deactivation by silylation. Below is given a typical procedure for benzene silylation and Wurtz coupling.†

References

1 P. K. Freman and L. L. Huthinson, *J. Org. Chem.*, 1980, **45**, 1924.
2 D. R. Weyenberg and L. H. Toporcher, *J. Am. Chem. Soc.*, 1962, **84**, 2843.

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† A mixture of 2.5 g Li (rolled into foil of 0.2 mm thickness with a few drops of mineral oil, cut into pieces of ~ 1 cm^2 and washed with THF), 13.3 ml benzene, 38.4 ml TMSCl, 120 ml THF and 0.5 g of **1** was irradiated with an immersed-type US apparatus (W_{max} = 30 W titanium resonator) in an argon atmosphere (22 kHz) below 300 °C (ice-cold water cooling). After 4 h of uninterrupted irradiation, Li almost completely dissolved. The mixture was poured into 250 ml of concentrated aqueous ammonia and the organic layer was dried over K_2CO_3 and evaporated on a rotary system giving almost pure **2**, 32.8 g (97%), solid crystalline mass, ^{1}H NMR, (δ/ppm) 0.5s (18H), 2.6m (2H), 5.7m (4H). With no catalyst the reaction took 40 h. Addition of 1 ml of liquid $TiCl_4$ reduced the yield of **2** to 25%. Thus, the metal in the resonator may only reduce the reaction rate.

A mixture of 2.5 g of Li foil, 38.4 ml TMSCl, 5 ml HMPA and 120 ml THF was irradiated as before for 4 h at 20–25 °C. Distillation gave 19.3 g of **3** (89.9%), ^{1}H NMR, (δ/ppm; CCl_4) 0.04s.