Bistrimethylsilylamidocopper: a Useful Reagent for Conversion of Aryl Iodides into Primary Aromatic Amines

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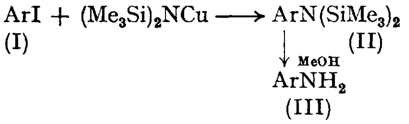
Summary Aryl iodides couple with $(Me_3Si)_2NCu$ to give $ArN(SiMe_3)_2$ compounds which, upon methanolysis, yield primary amines, $ArNH_2$.

We report a new method for converting aryl iodides (I) into the corresponding primary aromatic amines (III). Bistrimethylsilylamidocopper,[1] prepared *in situ* from hexamethyldisilazane, n-butyl-lithium and copper(I) iodide, couples with (I) in boiling pyridine (reaction time, *ca.* 18 h) to give moderate yields of silyl-protected amines (II). Treatment of (II) with methanol, after removal of solvent (optional) by distillation, gives (III) in quantitative yield.[2]



$$\begin{tikzcd} \mathrm{ArI} + (\mathrm{Me_3Si})_2\mathrm{NCu} \arrow[r] & \mathrm{ArN(SiMe_3)_2} \arrow[d, "\mathrm{MeOH}"] \\ \mathrm{(I)} & \mathrm{(II)} \\ & \mathrm{ArNH_2} \\ & \mathrm{(III)} \end{tikzcd}$$

Ar, % yield† of (II); Ph 60; *p*-$\mathrm{MeOC_6H_4}$, 45; p-$\mathrm{MeC_6H_4}$, 50; *o*-$\mathrm{ClC_6H_4}$, 30; *p*-$\mathrm{NO_2C_6H_4}$, 30; 2-Thienyl, 45.

Under comparable conditions, yields of (II) starting from aryl bromides—a preparatively more useful conversion—are considerably lower (10—15%); however, initial results at a higher temperature are promising. Thus in quinoline at 160°, bromobenzene reacts with $(\mathrm{Me_3Si})_2\mathrm{NCu}$ during 18 h to give $\mathrm{PhN(SiMe_3)_2}$ in 60% yield.

The reaction probably proceeds *via* direct displacement of aryl-bound halide by the bistrimethylsilylamido-group, in which co-ordination of halide to copper plays a crucial role. Rapid initial halide–amido-group exchange followed by coupling can be ruled out because phenylcopper reacts immediately with bromo-*NN*-bistrimethylsilylamine in tetrahydrofuran at 20° to give bromobenzene in high yield.

$$\mathrm{PhCu} + \mathrm{BrN(SiMe_3)_2} \longrightarrow \mathrm{PhBr} + \mathrm{CuN(SiMe_3)_2}$$

Despite some initial drawbacks, the simplicity of the method makes it an attractive alternative to the Grignard reagent plus methoxyamine technique and to conversions of non-activated aryl halides proceeding *via* aryne intermediates with their attendant isomer distribution problems.[3]

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† Isolated by distillation, not necessarily optimal.

[1] H. Bürger and U. Wannagat, *Monatsh.*, 1964, **95**, 1099.
[2] D. R. M. Walton, *J. Chem. Soc.* (*C*), 1966, 1706.
[3] M. S. Gibson in 'The Chemistry of the Amino Group,' Ed. S. Patai, Interscience, London, 1968, ch. 2.