

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

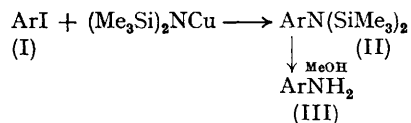
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Summary Aryl iodides couple with $(\text{Me}_3\text{Si})_2\text{NCu}$ to give $\text{ArN}(\text{SiMe}_3)_2$ compounds which, upon methanolysis, yield primary amines, ArNH_2 .

WE report a new method for converting aryl iodides (I) into the corresponding primary aromatic amines (III). Bistrimethylsilylamidocopper,¹ prepared *in situ* from hexa-

methyldisilazane, *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



Ar, % yield† of (II); Ph 60; *p*-MeOC₆H₄, 45; *p*-MeC₆H₄, 50; *o*-ClC₆H₄, 30; *p*-NO₂C₆H₄, 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 (Me₃Si)₂NCu during 18 h to give PhN(SiMe₃)₂ in 60% yield.

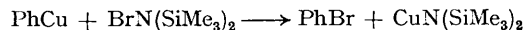
† Isolated by distillation, not necessarily optimal.

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.

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.



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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