SYNFACTS

Highlights in Current
Synthetic Organic
Chemistry

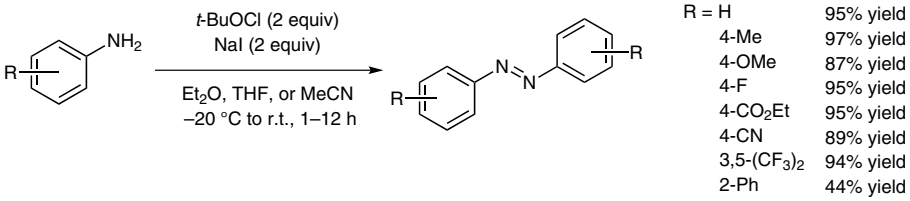
REPRINT

Thieme

Y. TAKEDA, S. OKUMURA, S. MINAKATA* (OSAKA UNIVERSITY, JAPAN)
Oxidative Dimerization of Aromatic Amines using *t*-BuOI: Entry to Unsymmetric Aromatic Azo Compounds
Angew. Chem. Int. Ed. **2012**, *51*, 7804–7808.

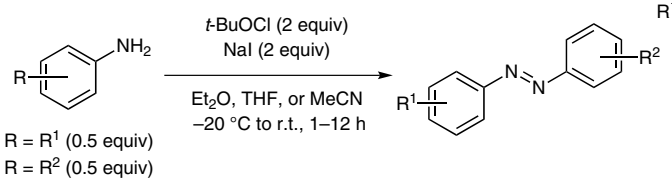
A Milder Route to Unsymmetric Azobenzenes

Homodimerization:



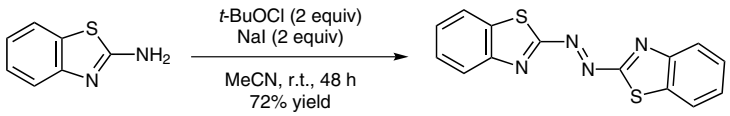
R = H	95% yield
4-Me	97% yield
4-OMe	87% yield
4-F	95% yield
4-CO_2Et	95% yield
4-CN	89% yield
3,5-$(CF_3)_2$	94% yield
2-Ph	44% yield

Cross-dimerization:



R^1 =	R^2 =	
4-Me	4-CO_2Et	62% yield
4-Me	4-C(O)Me	58% yield
4-Me	3-Cl	52% yield
4-C(O)Me	H	54% yield
4-C(O)Me	4-NO_2	72% yield
4-C(O)Me	4-F	61% yield

Homodimerization of heteroaromatic amines:



Significance: Azobenzenes have many diverse applications, ranging from organic dyes and indicators to liquid crystals and molecular photoswitches. While common synthetic routes require transition-metal oxidants, harsh reaction conditions or high reagent excess, the authors report mild reaction conditions to oxidatively dimerize substituted anilines to the azobenzenes using *tert*-butyl hypoiodite. Another advantage of this method is the significant improvement in yield when forming unsymmetric azobenzenes with two electron-withdrawing groups.

Comment: Although the mechanism is still nebulous, the authors provide evidence for the formation of an *N*,*N*-diiodoaniline which is then attacked by the remaining aniline. The subsequent loss of two equivalents of HI yields the azobenzene. The second equivalent of *tert*-butyl hypoiodite traps the HI to give *t*-BuOH and I_2.

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Category

Synthesis of Materials and Unnatural Products

Key words

azobenzenes

metal-free synthesis

oxidative dimerization