Unsymmetrical Biphenyl Synthesis using Copper(I) t-Butoxide

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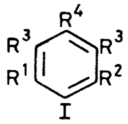
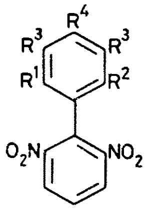
Summary The coupling of 1,3-dinitrobenzene with aryl iodides by copper(I) t-butoxide and pyridine provides a convenient route to 2,6-dinitrobiphenyls.

2,6-Dinitrobiphenyls have been prepared from aryl iodides by Ullmann condensation with 2,6-dinitrochlorobenzene,[1] and by reaction with 1,3-dinitrobenzene and copper(I) oxide in quinoline at 220—240 °C.[2] Neither method is attractive for larger-scale preparations; 2,6-dinitrochlorobenzene is expensive, and the harsh conditions of the alternative procedure give products contaminated from side-reactions and difficult to purify.

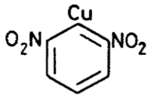
We find that copper(I) t-butoxide with pyridine mediates the reaction of aryl iodides with 1,3-dinitrobenzene to give 2,6-dinitrobiphenyls in mild conditions and in generally excellent yield. Operation on a large scale presents, moreover, no problem. Copper(I) t-butoxide may be prepared according to Saegusa *et al.*[3] and dissolved in pyridine, but it is more conveniently generated *in situ* by adding purified[4] copper(I) chloride to 1 mol of potassium t-butoxide in 1,2-dimethoxyethane ($1\ l\ mol^{-1}$). After 2—3 h pyridine (2—3 mol) is added, followed by 1,3-dinitrobenzene (0·83 mol). The red-purple solution-suspension is then ready for addition of aryl iodide. For example, addition of a slight excess of the aryl iodide (**1b**) was followed by heating under reflux for several hours. Precipitation with dilute hydrochloric acid, extraction with chloroform, filtration through alumina, evaporation, and recrystallization from methanol yielded the biphenyl (**2b**), 95% on dinitrobenzene, m.p. 117—118 °C (lit.[2] 117—119 °C). Oxygen was excluded from all operations before the work-up.



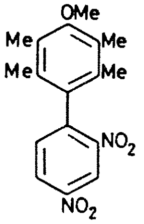
(**1**)



(**2**)



(**3**)



(**4**)

Table. Coupling of (**1**) with 1,3-dinitrobenzene to give (**2**)

	Aryl iodide (**1**)[a]				Yield of (**2**)[a]/%
	R^1	R^2	R^3	R^4	
a	H	H	H	H	87
b	H	H	H	OMe	95
c	H	H	H	NO_2	87
d	H	H	Bu^t	OMe	95
e	H	H	Cl	OMe	80
f	Me	H	Me	OMe	61
g	NO_2	H	H	H	40
h	Me	Me	Me	OMe	10[b]

[a] All products and all new compounds were characterised by elemental analysis and by spectrometry (mass, n.m.r.). Compounds (**1d**), (**1f**), (**1h**), (**2d**), (**2e**), (**2f**), (**2h**), and (**4**) are new.
[b] Using diglyme as solvent at 140 °C for 90 h.

Other yields are shown in the Table. 2,6-Dinitrophenylcopper(I) (**3**), or a complex thereof, is presumably an intermediate, and the 2,6-disubstituted aryl iodide (**1h**) seems to lie near the limit of accessibility to attack by this reagent. The 2,6-dinitrobiphenyl (**2h**) in this case was accompanied by a comparable amount of the isomeric 2,4-dinitrobiphenyl (**4**).

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[1] P. E. Fanta, *Synthesis*, 1974, 9.
[2] C. Björklund and M. Nilsson, *Acta. Chem. Scand.*, 1968, **22**, 2338.
[3] T. Tsuda, T. Hashimoto, and T. Saegusa, *J. Amer. Chem. Soc.*, 1972, **94**, 658.
[4] G. M. Whitesides, J. S. Sadowski, and J. Lilburn, *J. Amer. Chem. Soc.*, 1974, **96**, 2829.