A Convenient Synthesis of Symmetrical and Unsymmetrical Biphenyls by the Oxidation of *N*-Aryl-*N'*-(tri-*n*-butylstannyl)hydrazines

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Unsymmetrical biaryls are customarily prepared by the Gomberg reaction and its modification,[2] or by arylation with free radicals generated by the decomposition of aroyl peroxides.[2] However, yields of symmetrical biaryls as well as a mixture of isomeric unsymmetrical biaryls are usually below 50%. An alternate procedure is the photolysis of aromatic iodides in benzene solution, giving biaryls in 40—80% yields.[3] Recently, Taylor and his co-workers have reported the photolysis of arylthallium ditrifluoroacetates in benzene giving unsymmetrical biaryls in 80—90% yields.[4]

In this communication we report a new aromatic phenylation reaction which involves an oxidative decomposition of readily accessible *N*-aryl-*N'*-(tri-*n*-butylstannyl)hydrazines, prepared by transamination reaction from diethylaminotri-*n*-butylstannane and arylhydrazine in aromatic solvent. The transamination reaction proceeded usually above 90% as estimated from the amount of diethylamine evolved.

$$\mathrm{Bu_3SnNEt_2 + PhNHNH_2 \longrightarrow \underset{(I)}{Bu_3SnNHNHPh} + Et_2NH}$$

When I in benzene was oxidized with mercuric oxide at room temperature, a vigorous evolution of nitrogen took place quantitatively. Biphenyl was obtained in a 35% yield along with a 65% yield of diphenylmercury. Oxidation proceeds quantitatively. Of various metal oxides examined, silver oxide, manganese dioxide, and potassium permanganate proved to be also effective for oxidation. They liberated above 90% of the theoretical volume of nitrogen. Chromium trioxide and cuprous oxide liberated only a small amount of nitrogen under the same conditions. Oxidation of I with diethyl azodicarboxylate or mercury acetamide gave rise to the evolution of nitrogen in a nearly quantitative yield. Although the above reactions proceeded at room temperature, nitrogen was liberated quantitatively. The yield of biphenyl was usually below 30%. When the reaction of I (prepared from 15 mmol of diethylaminotri-*n*-butylstannane and an equimolar amount of phenylhydrazine) with chloranil (20 mmol) was carried out in benzene (300 m*l*) at room temperature, the yield of biphenyl increased to 93%. In an attempt to extend this type of phenylation reaction, similar oxidation of I with chloranil in anisole and pyridine were tried. The results are summarized in the following Table. It is noteworthy that, in pyridine, the oxidative decomposition of I proceeded even at −35°C giving a mixture of phenylpyridines in high yield along with nitrogen. Each mixture of isomeric phenylpyridines and methoxybiphenyls obtained was identical in composition with those observed on other free-radical phenylation of pyridine[5] and anisole.[6] The results suggest that the oxidation of I produced phenyl radicals, which in turn attacked the solvent to form biaryls. The reaction can be represented as follows. Similarly, when *N*-*p*-tolyl-*N'*-(tri-*n*-butylstannyl)hydrazine prepared from diethylaminotri-*n*-butylstannane and *p*-tolyl-hydrazine by transamination reaction was oxidized with chloranil in benzene, *p*-methylbiphenyl was formed in high yield. The yields and isomer distributions are given in the following Table.[4]

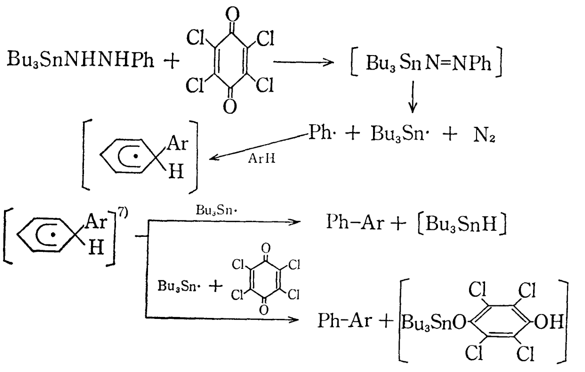

TABLE THE OXIDATION OF *N*-ARYL-*N'*-(TRI-*n*-BUTYLSTANNYL)HYDRAZINES WITH CHLORANIL IN AROMATIC SOLVENTS

Ar	Solvent	Reaction temperature	Yield of biaryls[a] (%)
Phenyl	Benzene	Room temp.	93
	Anisole	−15°——10°	89[c]
	Pyridine	−35°	*ca.* 90[b]
p-Tolyl	Benzene	Room temp.	85[d]

a) Purity of products was determined by glc. The identity of products was established by chromatographic comparison with authentic samples. b) Composition: 64.1% *o*-methoxybiphenyl, 22.5% *m*-methoxybiphenyl, 13.4% *p*-methoxybiphenyls. c) Composition: 59% α-phenylpyridine, 41% β-phenylpyridine. d) Composition: 93.3% *p*-methylbiphenyl, 6.2% *p,p'*-dimethyl-biphenyl, 0.5% biphenyl.

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[2] See, for example: a) W. E. Bachmann and R. A. Hofman, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York (1944), p. 224: b) O. C. Dermer and M. T. Edison, *Chem. Rev.*, **57**, 77 (1957): c) D. R. Augood and G. H. Williams, *ibid.* **57**, 123 (1957).

[3] W. Wolf and N. Kharasch, *J. Org. Chem.*, **30**, 2493 (1965).

[4] E. C. Taylor, F. Kienzle, and A. McKillop, *J. Amer. Chem. Soc.*, **92**, 6088 (1970).

[5] K. Schofield, "Hetero-Aromatic Nitrogen Compounds," Butterworths, Washington, D. C., and London (1967), p. 253.

[6] T. Suehiro, *Nippon Kagaku Zasshi*, **72**, 1070 (1951).

[7] As shown in the equation, two pathways are conceivable for the hydrogen abstraction form intermediate, arylcyclohexadienyl radical. Since the reaction mixture was treated with aqueous potassium hydroxide in order to remove tetrachlorohydroquinone, tributyltin hydride and tributyltin 4-hydroxyl-2,3-5,6-tetrachlorophenoxide might be hydrolyzed to tributyltin hydroxide which was isolated as major tin-containing component.