

distilled; ot $\sim 125^\circ\text{C}/0.04\text{ mmHg}$. R_f : 0.10 (hexanes). $^1\text{H NMR}$: δ 0.02 (s, 3 H), 0.04 (s, 3 H), 0.89 (s, 9 H), 0.88–0.97 (m, 2 H), 1.26–1.50 (m, 8 H), 4.05 (m, 1 H), 4.27 (t, $J = 3.7\text{ Hz}$, $^1J_{\text{SiH}}$ = 192 Hz, 2 H), 5.00 (d (br), $J = 10.9\text{ Hz}$, 1 H), 5.11 (d (br), $J = 17.3\text{ Hz}$, 1 H), 5.71–5.84 [ddd (not resolved), $J = 6.0, 10.3$, and 16.8 Hz , 1 H], 7.30–7.42 (m, 3 H), 7.51–7.59 (m, 2 H). $^{13}\text{C NMR}$ (APT): δ -4.87 (SiMe), -4.43 (SiMe), 9.90 (CH_2), 18.22 (CMe_3), 24.72 (CH_2), 24.98 (CH_2), 25.86 (CMe_3), 32.75 (CH_2), 37.90 (CH_2), 73.83 (CH), 113.45 ($=\text{CH}_2$), 127.97, 129.49 (C_{para}), 132.76 (C_{ipso}), 135.22, 141.90 ($=\text{CH}$). IR (thin film): 2928 (s), 2856 (m), 2133 (s), 938 (m), 837 (s), 775 (m), 700 (m) cm^{-1} . LRMS [CI^+ (CH_4)] m/z (relative intensity): 347 (0.8), 181 (100). Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{OSi}_2$ (348.68): C, 68.90; H, 10.41. Found: C, 69.17; H, 10.54.

8-(Phenylsilyl)-3-phenyloxy-1-ene (24b). Yield: 90.0 mg (31%, 95% pure by GC) of 24b as a colorless oil. Kugelrohr distillation gave 82.0 mg (28%, 96% pure by GC); ot $\sim 130^\circ\text{C}/0.04\text{ mmHg}$. R_f : 0.30 (hexanes). $^1\text{H NMR}$: δ 0.87–0.97 (m, 2 H), 1.14–1.50 (m, 6 H), 1.63–1.74 (m, 2 H), 3.18–3.27 (m, 1 H), 4.29 (t, $J = 3.7\text{ Hz}$, $^1J_{\text{SiH}}$ = 191 Hz, 2 H), 4.97–5.06 (m, 2 H), 5.88–6.02 (m, 1 H), 7.16–7.43 (m, 8 H), 7.54–7.59 (m, 2 H). $^{13}\text{C NMR}$ (APT): δ 9.92 (CH_2), 24.89 (CH_2), 27.06 (CH_2), 32.68 (CH_2), 35.23 (CH_2), 49.86 (CH), 113.88 ($=\text{CH}_2$), 126.09 (C_{para}), 127.58, 127.97, 128.42, 129.49 (C_{para}), 132.73 (C_{ipso}), 135.22, 142.49, 144.61 (C_{ipso}). IR (thin film): 3067 (w), 3026 (w), 2924 (s), 2854 (m), 2131 (s), 1116 (m), 937 (s), 847 (s), 737 (m), 699 (s) cm^{-1} . HRMS: calcd for $\text{C}_{20}\text{H}_{26}\text{Si}$, 294.1804, found 294.1802. LRMS (EI) m/z (relative intensity): 294 (1), 118 (46), 117 (100), 107 (45). Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{Si}$: C, 81.57; H, 8.90. Found: C, 81.76; H, 9.01.

2-Deuterio-3-phenyl-1-(phenyldideuteriosilyl)propane. Yield: 122.6 mg (0.53 mmol, 76%, >99% pure by GC); ot $\sim 100^\circ\text{C}/0.04\text{ mmHg}$. R_f : 0.33 (hexanes). $^1\text{H NMR}$: δ 0.97 (d, $J = 8.3\text{ Hz}$, 2 H), 1.77 [quint, t (not resolved)], $^3J_{\text{H,H}} = 8.0\text{ Hz}$, $^2J_{\text{H,D}} = 1.8\text{ Hz}$, 1 H], 2.67 (d, $J = 7.6\text{ Hz}$, 2 H), 7.13–7.43 (m, 8 H), 7.53–7.59 (m, 2 H). $^{13}\text{C NMR}$ (APT): δ 9.42 (CH_2Si), 26.52 [t, $^1J_{\text{C,D}} = 19.8\text{ Hz}$ (CHD)], 38.82 (CH_2Ph), 125.76 (C_{para}), 127.99, 128.27, 128.51, 129.57 (C_{para}), 132.37 (C_{ipso}), 135.23, 142.10 (C_{ipso}). IR (thin film): 3065 (m), 3025 (m), 2917 (s), 1557 (s), 1495 (m), 1453 (m), 1428 (m), 1115 (m), 738 (s), 697 (s), 640 (m), 624 (m), 595 (m) cm^{-1} . HRMS: calcd for $\text{C}_{15}\text{H}_{15}\text{D}_3\text{Si}$, 229.1366, found 229.1363. LRMS (EI) m/z (relative intensity): 229 (1.1), 228 (1.2), 109 (100), 91 (79). Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{D}_3\text{Si}$ (229.41): C, 78.53; H, 7.91 (H plus D as H). Found: C, 78.30; H, 7.94 (H plus D as H).

Acknowledgment. We thank the National Institutes of Health and the German Academic Exchange Service (DAAD) for their generous support of this research and Dr. Kevin Bobbitt for performing the $^2\text{H NMR}$ spectra.

Supplementary Material Available: Experimental and spectroscopic data for starting materials phenyltrideuteriosilane, 13, 19b, 19c, 19d, and $\text{Cp}_2^*\text{YCH}(\text{SiMe}_3)_2$ (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

2-Arylbenzoxazole Formation through *o*-Fluoro Displacement Reactions

Robert J. Perry* and B. David Wilson

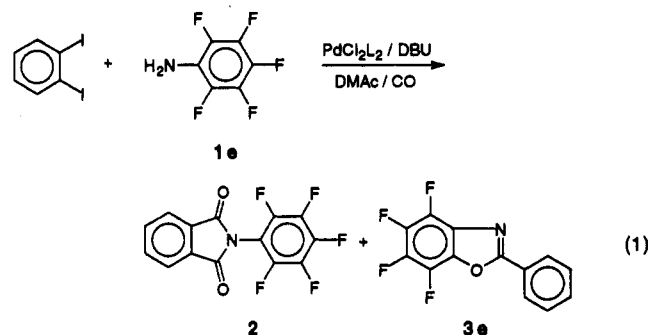
Corporate Research Laboratories, Eastman Kodak Company, Rochester, New York 14650-2110

Received March 30, 1992 (Revised Manuscript Received July 28, 1992)

Recently, a novel method for the formation of *N*-substituted phthalimides via the palladium-catalyzed carbonylation and condensation of aryl diiodides and primary amines was reported.¹ The method was a general one and

provided easy access to phthalimides with common electron-donating and -withdrawing substituents. The general scope of this reaction suggested that the use of highly deactivated amines might also give the desired phthalimides. Interest has been generated over polymeric materials containing fluorine, which have been shown to possess good thermooxidative stability as well as increased solubility and processability.² Perfluorinated aromatic amines are poor nucleophiles and as such have found limited utility in the preparation of high-performance materials such as polyimides and aramids.³ Described herein are the results of an investigation into the palladium-catalyzed carbonylation and condensation of iodoaromatics and fluorinated anilines.

A reaction was run in which a DMAc solution containing *o*-diiodobenzene, pentafluoroaniline (1e), 1.2 equiv of DBU, and 3% PdCl_2L_2 (where $\text{L} = \text{PPh}_3$) were allowed to react under 95 psig of carbon monoxide (CO) at 115°C (eq 1).



After 22 h, the reaction mixture showed the presence of a small amount of the desired *N*-(pentafluorophenyl)-phthalimide 2 but also a number of other products. The major constituent of the reaction mixture was determined to be 2-phenyl-4,5,6,7-tetrafluorobenzoxazole (3e).

A probable route for the formation of 3e is shown in Scheme I. In this reaction, palladium(0) oxidatively adds to the aryl iodide and then inserts CO to give the acyl-palladium complex 4 (ligands on Pd are omitted for clarity). Complex 4 is attacked by pentafluoroaniline to give iodoamide intermediate 5. The amide nitrogen in 5 is relatively non-nucleophilic, and when the other aryl-iodide bond is activated by palladium, only a small portion undergoes CO insertion and subsequent attack by the amide nitrogen producing the imide 2 (path a). A majority of 5 undergoes reduction and amide 6e is formed. With heating, and in the presence of base, 6e slowly cyclized with displacement of fluoride to give the observed benzoxazole 3e (path b). Alternately, cyclization of the benzoxazole may precede reduction of the aryl-iodide bond, although no 2-(2'-iodophenyl)-4,5,6,7-tetrafluorobenzoxazole was observed.

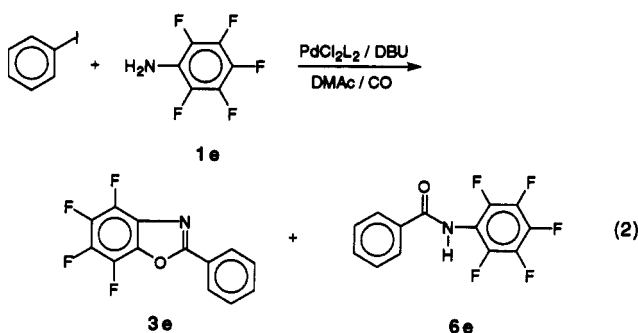
If 6e were an intermediate, then an alternate method for making 3e would be to start with iodobenzene and

(1) Perry, R. J.; Turner, R. S. *J. Org. Chem.* 1991, 56, 6573.

(2) (a) Oishi, Y.; Harada, S.; Masaaki, K.; Imai, Y. *J. Polym. Sci. Polym. Chem. Ed.* 1989, 27, 3393 and references cited therein. (b) Cassidy, P. E. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* 1990, 31(1), 338. (c) McGrath, J. E.; Grubbs, H.; Rogers, M. E.; Mercier, R.; Joseph, W. A.; Alston, W.; Rodriguez, D.; Wilkes, G. L. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* 1991, 32(2), 103. (d) Matsuura, T.; Hasuda, Y.; Nishi, S.; Yamada, N. *Macromolecules* 1991, 24, 5001. (e) Harris, F. W.; Hsu, S. L. C.; Tsao, C. C. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* 1990, 31(1), 342. (f) Mercer, F. W.; Goodman, T. D. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* 1991, 32(2), 189.

(3) (a) Hougham, G.; Shaw, J.; Tesoro, G. In *Polyimides: Materials, Chemistry and Characterization*; Feger, C.; Khojasteh, M. M., McGrath, J. E., Eds.; Elsevier: New York, 1989; pp 465–478. (b) Hougham, G.; Tesoro, G.; Shaw, J. *Polym. Mater. Sci. Eng.* 1989, 61, 369.

pentafluoroaniline. Such a reaction was run (eq 2), and



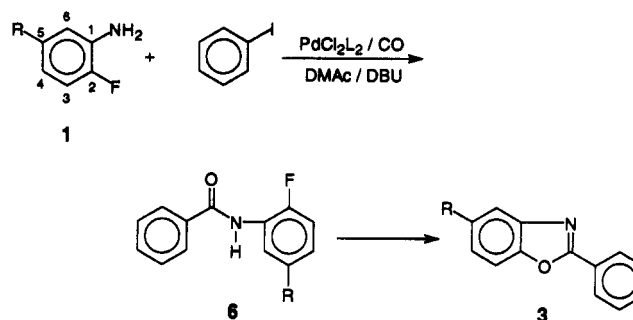
N-phenyltetrafluorobenzoxazole (3e) was formed in addition to the expected benzamide 6e in a 1:2 ratio. This result suggested that *o*-fluoro displacement in *N*-arylbenzamides might provide a general route to the 2-arylbenzoxazole ring system.

Several reports have appeared in which polybenzoxazoles were prepared by the displacement of *o*-nitro,⁴ -nitrilo,⁵ -fluoro, -bromo, and -chloro^{4,6} substituents on aramids. These techniques required the use of high temperatures (>300 °C). Polybenzoxazoles were also prepared by the displacement of *o*-methoxy groups in a similar thermal process.⁷ An alternate method of benzoxazole formation was the displacement of an *o*-chloro group in a benzyne reaction.⁸ A lower temperature, base-induced method for *o*-fluoro displacement was demonstrated by Kobayashi et al.⁹ in which 6e was treated with NaH in refluxing DMF to give tetrafluorobenzoxazole 3e. This method was confined solely to perfluoroaniline, though, and we wished to see if our cyclization reaction could be extended to other *o*-fluoroaniline derivatives.

The reaction of *o*-fluoroaniline and iodobenzene at 115 °C in the presence of 1.2 equiv of DBU, 3% PdCl₂L₂, and 95 psig of CO gave only amide 6a (Table I). There was no evidence for spontaneous cyclization to 2-phenylbenzoxazole (3a). The same observation was noted for the difluoro, trifluoromethyl, and methyl derivatives 6b, 6c, and 6d. Isolated yields of these intermediate amides were fair to good as shown in Table I. Only the pentafluoro derivative 6e exhibited any propensity to cyclize under these conditions. To determine whether cyclization would occur independently, several of these amides were subjected to NaH cyclization conditions described by Kobayashi.⁹ In the presence of 1.8–1.9 equiv of NaH in refluxing DMF, 6c and 6e completely cyclized within 1 h. After 36 h, 6a was only 85% cyclized and amide 6b only 40%. When amides 6c and 6e were treated with 2 equiv of DBU, rather than NaH, in refluxing DMF facile cyclization to the benzoxazole occurred.

The latter two experiments suggested that excess DBU present in the reaction mixture at the outset might provide an ideal way to cyclize the readily formed amides. To this end, pentafluoroaniline 1e and iodobenzene were allowed

Table I. Preparation of *o*-Fluoroamides and Benzoxazole



entry	aniline	amide 6 ^a		benzoxazole 3 ^a	
		yield (%)	mp (°C)	yield (%)	mp (°C)
a	1a, R = H	74 ^b	108–109	c	
b	1b, R = F	95 ^b	112–114	43 ^d	104.5–105
c	1c, R = CF ₃	37 ^{b,e}	131–131.5	87 ^f	85.5–86
d	1d, R = CH ₃	83 ^b	117–118.5	c	
e	1e, R = F ₅	43 ^{b,h}	181–182	62 ⁱ	120–121.5
f	1f, R = F ₄ ^j	75 ^k	138.5–139	c	
g	1g, R = F ₃ ^l	87 ^k	139–140	c	
h	1h, R = NO ₂	m		43 ^m	170.5–171.5

^a Yields of isolated, purified products. ^b Amide isolation from carbonylation and coupling reaction at 115 °C with 1.2 equiv of DBU. ^c <5% Benzoxazole formed after 24 h at 190 °C with 4 equiv of DBU. ^d Benzoxazole isolated after 3 days at 210 °C with 4.4 equiv of DBU. ^e Very slow coupling reaction at 115 °C; starting (trifluoromethyl)aniline still present after 24 h. ^f Benzoxazole isolated after 24 h at 165 °C with 4 equiv of DBU. ^g Pentafluoroaniline. ^h 18% Benzoxazole also isolated. ⁱ Benzoxazole isolated after 3 h at 165 °C with 2.2 equiv of DBU. ^j 2,3,4,5-Tetrafluoroaniline. ^k Amide isolated after 24 h at 190 °C with 4 equiv of DBU. ^l 2,4,5-Trifluoroaniline. ^m Only benzoxazole isolated after 0.75 h at 175 °C with 4.4 equiv of DBU.

to react for 3 h in the presence of 1.5% PdCl₂L₂, 95 psig of CO, and 2.2 equiv of DBU at 165 °C in DMF. After this time, complete cyclization to the tetrafluorobenzoxazole had occurred, from which a 62% yield of 3e was obtained. (Trifluoromethyl)aniline 1c and iodobenzene were allowed to couple at 150 °C for 16 h after which time the temperature was raised to 175 °C (refluxing DMF). The elevated initial temperature increased the relatively slow rate of amide formation as well as facilitated the cyclization that was complete in an additional 6 h at the higher temperature. An 87% yield of the 5-(trifluoromethyl)benzoxazole was obtained. Nitrofluoroaniline 1h also cyclized to give 43% of 5-nitro-2-phenylbenzoxazole (3h). The less electron-poor anilines 1a,b,d,f–g did not respond as favorably. The difluorinated amide 6b could be forced to cyclize only under very harsh conditions (3 days at 210 °C), and even then only 43% benzoxazole was isolated. The other substituted anilines gave good yields of the amides but did not cyclize even after 24 h at 190 °C in the presence of 4 equiv of DBU.

The presence of a *p*-methoxy group on iodobenzene, which should increase the nucleophilicity of the amidate oxygen in 6i, also failed to induce cyclization, and only amide was isolated (Table II). The methoxy group in the iodobenzene did not hinder subsequent benzoxazole formation. Reaction of the same *p*-iodoanisole with the more electron-deficient pentafluoroaniline gave 68% of the corresponding tetrafluorobenzoxazole 3j. Other strongly electron-deficient *o*-fluoroanilines reacted with *p*-iodoanisole to give anisyl derivatives 3k,l. In the nitro case, 3l, the benzoxazole product was isolated as the 5-amino-substituted derivative. The lengthy reaction time (24 h) compared to that of 3h (1 h) allowed the palladium catalyst to reduce the nitro group as has been reported.¹⁰

(4) (a) Pearce, E. M. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* 1989, 30(1), 344. (b) Kim, S.; Pearce, E. M. *Makromol. Chem.* 1989, 15, 187 and references cited therein.

(5) Kim, S.; Pearce, E. M.; Kwei, T. K. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* 1987, 28(1), 47.

(6) Shinra, K.; Shono, T.; Matsumura, S.; Asano, N.; Eguchi, M.; Izumi, M. *Japanese Pat. Appl.* No. 45018875, June 27, 1970.

(7) Mueller, W. H.; Erckel, R. J.; Khanna, D. N. *South African Pat. Appl.* No. ZAP87/09543 Dec 21, 1987.

(8) El-Sheikh, M. I.; Marks, A.; Biehl, E. R. *J. Org. Chem.* 1981, 46, 3256.

(9) (a) Inukai, Y.; Oono, Y.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* 1979, 52, 516. (b) Inukai, Y.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* 1979, 52, 2657.

Scheme I

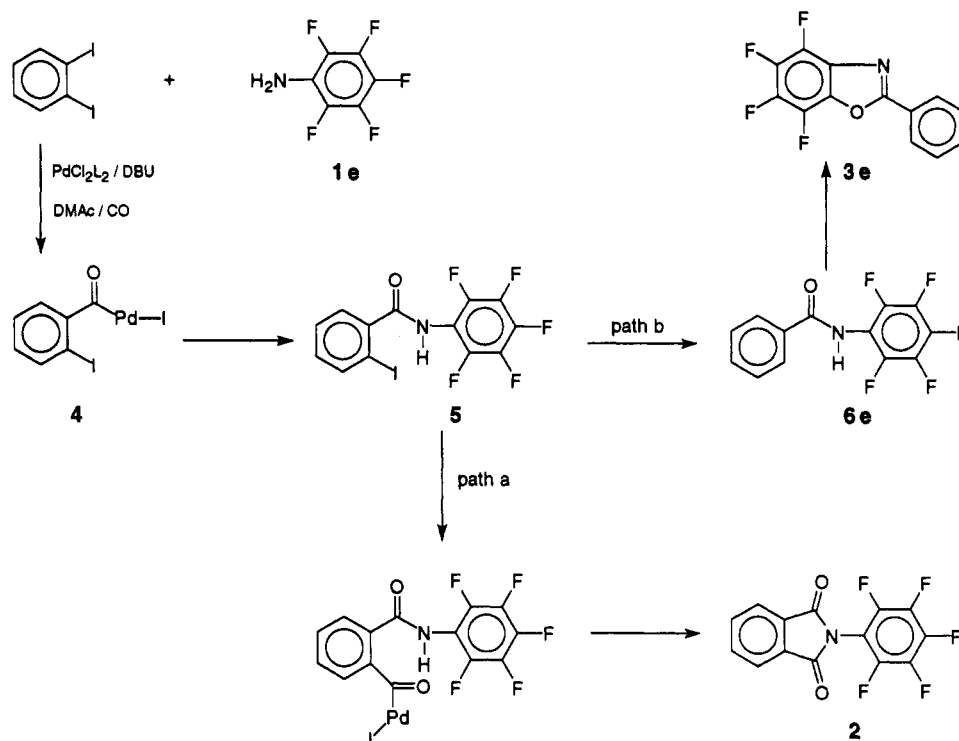
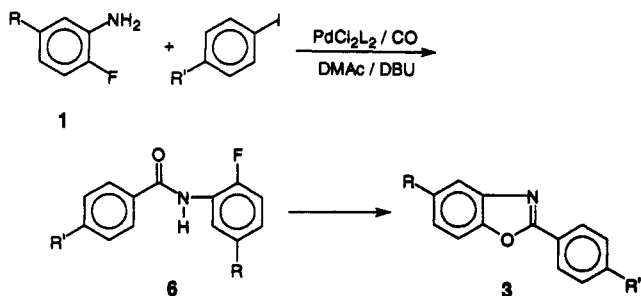


Table II. Preparation of Benzoxazoles from Substituted Aryl Iodides



entry	aniline	aryl iodide	amide 6 ^a		benzoxazole 3 ^a	
			yield (%)	mp (°C)	yield (%)	mp (°C)
i	1a	R' = OCH ₃	60 ^b	138.5–139	c	134–134.5
j	1e	R' = OCH ₃			68 ^d	70 ^e
k	1c	R' = OCH ₃			70 ^e	101–193
l	1h	R' = OCH ₃			38 ^f	152–154
m	1e	R' = CN			59 ^g	152–154
n	1e	R' = CN			81 ^h	183–185
o	1h	R' = CN			38 ⁱ	238–242

^a Yield of isolated, purified products. ^b Amide isolated after 22 h at 175 °C with 4.2 equiv of DBU. ^c <5% Benzoxazole formed after 22 h at 175 °C with 4.2 equiv of DBU. ^d Benzoxazole isolated after 3.5 h at 160 °C with 2.4 equiv of DBU. ^e Benzoxazole isolated after 24 h at 165 °C with 4 equiv of DBU. ^f 5-Amino-substituted benzoxazole isolated after 25 h at 175 °C with 4 equiv of DBU. ^g Benzoxazole isolated after 2 h at 160 °C with 2.2 equiv of DBU. ^h Benzoxazole isolated after 16 h at 165 °C with 4 equiv of DBU. ⁱ 5-Amino-substituted benzoxazole isolated after 24 h at 175 °C with 4 equiv of DBU.

Changing the substituent on iodobenzene to a cyano moiety had little effect on the outcome of the reaction. Entries m–o show that amidation and cyclization occurred

readily to give fair to good yields of products. Again, the nitro group was reduced to the amine.

In summary, the intramolecular displacement of *o*-fluoro groups to form 2-arylbenzoxazoles from amides derived from *o*-fluoroanilines and iodoaromatics is effective if the anilines are extremely electron deficient. With less electron-poor anilines, harsh conditions must be employed to effect cyclization, and with unactivated anilines, no benzoxazole is formed.

Experimental Section

Reactions were run in a 120-mL glass pressure reaction vessel outfitted with a stirbar, a pressure gauge, a pressure release valve, a gas inlet, and a straight ball valve for degassing and sample withdrawal in a well-ventilated hood behind safety shields. All reactions were run at 0.33 M in *N,N*-dimethylacetamide (DMAc) or *N,N*-dimethylformamide (DMF) at 115–160 °C under 95 psig of CO using 1.5–3% PdCl₂L₂ (L = PPh₃) as the catalyst system.

All reactions were monitored on a gas chromatograph as reported previously.¹ ¹H and ¹³C NMR spectra were acquired on a 300-MHz spectrometer using CDCl₃ as both solvent and internal reference. Fourier transform infrared spectra were recorded as KBr pellets. Chromatography was performed on a radial layer chromatographic device using 4-mm PF-254 silica gel plates.

Carbon Monoxide (CO, Air Products, UPC grade), anhydrous DMAc, anhydrous DMF, pentafluoroaniline, $\alpha,\alpha,\alpha,6$ -tetrafluoro-*m*-toluidine, 2,5-difluoroaniline, *o*-fluoroaniline, 2-fluoro-5-methylaniline, 2,3,4,5-tetrafluoroaniline, 2,4,5-trifluoroaniline, 2-fluoro-5-nitroaniline, NaH (60% suspension in mineral oil), bis(triphenylphosphine)palladium(II) chloride (PdCl₂L₂) (all Aldrich), 4-iodoanisole, and 4-iodobenzonitrile (both from Eastman Kodak Company) were all used as received. Iodobenzene, *o*-diiodobenzene (both Kodak), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Aldrich) were fractionally distilled under reduced pressure.

Representative examples of benzamide and benzoxazole formation are given below.

***N*-(2,5-Difluorophenyl)benzamide (6b).** A pressure vessel was charged with iodobenzene (1.0 mL, 8.94 mmol), 1b (900 μ L, 8.94 mmol), PdCl₂L₂ (94 mg, 0.134 mmol), and DMAc (27 mL), degassed and purged with argon, and then degassed and pressurized with CO. After the contents had dissolved, DBU (1.60 mL, 10.7 mmol, 1.2 equiv) was added and the reaction was allowed

(10) (a) Min'kov, A. I.; Eremenko, N. K.; Merkur'eva, S. E.; Efimov, O. A. *Izv. Akad. Nauk SSSR (Transl. Ed., Engl.)* 1986, 1223. (b) Heck, R. F. In *Palladium Reagents in Organic Syntheses*; Academic Press: San Diego, 1985; pp 418–419.

to proceed at 115 °C under 95 psig of CO for 3 h. After this time the reaction mixture was concentrated in vacuo and the residue extracted with hot toluene (3 × 50 mL). The toluene extracts were combined and concentrated to dryness, and the pale yellow solid was dissolved in toluene and filtered through a short silica gel column eluting with toluene. The product was collected, concentrated, and recrystallized from ethanol/water to give 1.98 g product (95%); mp 112–114 °C; IR (KBr) 3330, 1666, 1626, 1536, 1477, 1443, 1325, 1245, 1201, 871, 734 cm⁻¹. Anal. Calcd for C₁₃H₉F₂NO: C, 66.95; H, 3.89; N, 6.01. Found: C, 67.01; H, 3.88; N, 5.96.

6-Fluoro-2-phenylbenzoxazole (3b). Iodobenzene (1.0 mL, 8.94 mmol), 1b (910 μL, 8.94 mmol), PdCl₂L₂ (94 mg, 0.134 mmol), DBU (6.0 mL, 40.0 mmol, 4.2 equiv), and DMF (27 mL) were allowed to react at 155–160 °C and 95 psig of CO for 16 h. The temperature was then raised to 210 °C and allowed to remain there for 3 days. After this time, GC analysis of the reaction mixture indicated that >95% cyclization had taken place. The reaction mixture was filtered, concentrated, dissolved in a toluene/chloroform mixture, and passed through a short column of silica gel (eluting with toluene), and the product fraction was collected and then concentrated again. The product was recrystallized from methanol/water to give 820 mg (43%) of colorless crystals: mp 104.5–105 °C; IR (KBr) 1625, 1557, 1480, 1345, 1290, 1128, 1103, 1050, 1022, 957, 838, 770, 700, 685 cm⁻¹. Anal. Calcd for C₁₃H₉FNO: C, 73.23; H, 3.78; N, 6.57. Found: C, 73.09; H, 3.98; N, 6.74.

Acknowledgment. We thank J. Lugert for GC-MS data and P. Keogh for their interpretation, W. Lenhart and M. Goodberlet for NMR spectra, and D. Margevich for FTIR spectra.

Supplementary Material Available: Experimental details and physical and spectral properties of all amides and benzoxazoles synthesized (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

An Improved Method for the Preparation of Pyrrolidines by the Cycloaddition of Nonstabilized 2-Azaallyl Anions with Alkenes

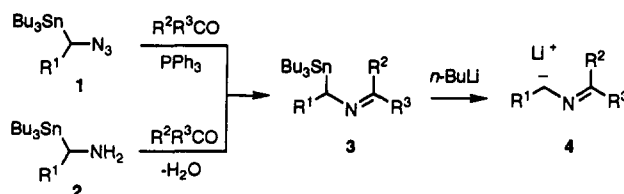
William H. Pearson* and Michael J. Postich

Department of Chemistry, Willard H. Dow Laboratories,
The University of Michigan, Ann Arbor, Michigan 48109

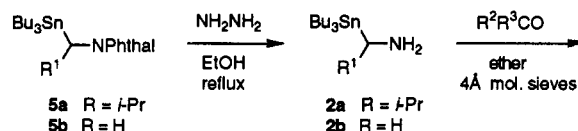
Received June 23, 1992

We have previously shown that nonstabilized 2-azaallyl anions 4 may be generated by the transmetalation of (2-azaallyl)stannanes 3. These anions were found to undergo efficient [$\pi 4s + \pi 2s$] cycloaddition reactions with certain alkenes to afford pyrrolidines after quenching with an electrophile.^{1,2} The imines 3 were prepared in good yield from azides 1 by an aza-Wittig reaction with aldehydes or ketones. However, this method was limited to *N*-(trialkylstannyl)methanimines (3, R¹ = H), since azides 1 were found to be thermally unstable where R¹ = alkyl. This limitation prevented the study of nonstabilized 1,3-disubstituted 2-azaallyl anions. We now wish to report that

(2-azaallyl)stannanes 3 may be more conveniently prepared from (1-aminoalkyl)stannanes 2 and that these imines increase the scope of the 2-azaallyl anion route to pyrrolidines.



Initial attempts to prepare (1-aminoalkyl)stannanes 2 by the reduction of azides or nitriles or by reductive amination of stannyl ketones were unsuccessful.^{1b} However, Chong recently reported the synthesis of these amines by deprotection of phthalimides 5, obtained by a Mitsunobu reaction on α -hydroxystannanes.³ We prepared phthalimides 5a³ and 5b, which were deprotected with hydrazine to afford the amines 2a³ and 2b. Although 5b could be prepared by the Mitsunobu route, it was more conveniently prepared by *N*-alkylation of potassium phthalimide. Without purification, the amines 2a and 2b were condensed with isobutyraldehyde, acetone, and cyclopentanone in the presence of molecular sieves to give the (2-azaallyl)stannanes 3a–d in good yield after distillation. The preparation of 3a–3c illustrates the superiority of this method to the aza-Wittig approach in the preparation of branched (2-azaallyl)stannanes. In addition, although imines such as 3d may be prepared by the aza-Wittig reaction,^{1b} the current method is more convenient.



	R ¹	R ²	R ³	Overall Yield from 5
3a	<i>i</i> -Pr	H	<i>i</i> -Pr	79%
3b	<i>i</i> -Pr	CH ₃	CH ₃	84%
3c	<i>i</i> -Pr	-(CH ₂) ₄ -	-	75%
3d	H	-(CH ₂) ₄ -	-	86%

Transmetalation of (2-azaallyl)stannanes 3a and 3b in the presence of various anionophiles led to smooth cycloaddition reactions (Table I). To facilitate isolation, the *N*-methylpyrrolidine derivatives were prepared by quenching the *N*-lithiopyrrolidines with iodomethane. Other electrophiles (e.g., H₂O or *p*-TsCl) have been used previously to generate *N*-unsubstituted or *N*-protected pyrrolidines.^{1b} Imines such as 3d have been used previously in cycloaddition reactions.^{1b}

The ability to generate more highly substituted nonstabilized 2-azaallyl anions provides the first information on the geometry of such anions.⁴ Cycloadditions of the anion derived from imine 3a produce only a *cis* relationship between the 2- and 5-substituents. This is consistent with a reaction proceeding through the "W"-form of the anion, assuming the "U"-form may be ruled out on steric grounds.

(3) Chong, J. M.; Park, S. B. *J. Org. Chem.* 1992, 57, 2220–2222.

(4) Although unstabilized 1,3-disubstituted 2-azaallyl anions have not been generated, 1,3-diaryl-2-azaallyl anions have been studied and are proposed to react in the "W"-form. See ref 2a and: (a) Eidenschink, R.; Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* 1972, 11, 292. (b) Young, R. N.; Ahmad, M. A. *J. Chem. Soc., Perkin Trans. 2* 1982, 35. (c) Pearson, W. H.; Walters, M. A.; Osweil, K. D. *J. Am. Chem. Soc.* 1986, 108, 2769–2771 and references cited therein. (d) Andrews, P. C.; Mulvey, R. E.; Clegg, W.; Reed, D. J. *Organomet. Chem.* 1990, 386, 287–297.

(1) (a) Pearson, W. H.; Szura, D. P.; Harter, W. G. *Tetrahedron Lett.* 1988, 29, 761–764. (b) Pearson, W. H.; Szura, D. P.; Postich, M. J. *J. Am. Chem. Soc.* 1992, 114, 1329–1345.

(2) For reviews on 2-azaallyl anion cycloadditions, see: (a) Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* 1974, 13, 627–639. (b) Pearson, W. H. In *Studies in Natural Products Chemistry*; Atta-ur-Rahman, Ed.; Elsevier: Amsterdam, 1988; Vol. 1, pp 323–358.