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Copper Salt Catalyzed Addition of Arylboronic Acids to Azodicarboxylates

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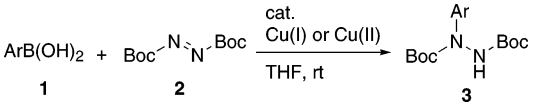
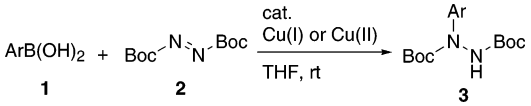


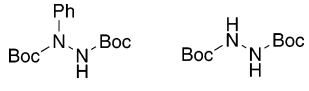
The addition of arylboronic acids **1** to azodicarboxylates **2** in the presence of a catalytic amount of a copper salt under mild reaction conditions gives aryl-substituted hydrazines **3** in high yields. The reaction is tolerant of a wide variety of functional groups.

Aromatic amines are components of many classes of biologically active molecules, and because of this, they are key intermediates in the synthesis of a variety of aromatic compounds.[1] A variety of methods have been developed for the preparation of aromatic amines. Azodicarboxylates have been used in the preparation of hydrazines,[2] which are useful precursors in the synthesis of amines.[3] The direct amination of arenes with azodicarboxylates is one of a number of attractive methods for the preparation of aryl-substituted hydrazines. However, the reaction is limited to electron-rich arenes because the reaction proceeds via an electrophilic substitution.[4] The addition of organometallic reagents (Mg,[5] Li,[5,6] and Zn[7]) to azodicarboxylates is also a straightforward method for the preparation of hydrazine derivatives. Organoboronic acids are widely available, relatively inert to air and water, and thermally stable. For these reasons, boronic acids can be readily handled in the laboratory without the need for special precautions. Most importantly, they tolerate a wide range of functional groups, an important issue in organic synthesis. We wish to report the copper salt-catalyzed addition of arylboronic acids **1** to azodicarboxylates **2** under mild reaction conditions leading to the production of aryl-substituted hydrazines **3** in high yields (Scheme 1). The reaction tolerates a wide variety of functional groups. The preparation of aryl-substituted hydrazines by the $Cu(OAc)_2$-catalyzed reaction of Boc-NHNHBoc with arylbismuth compounds was recently reported.[8] Kabalka also reported on an efficient synthetic method for preparing aryl-substituted hydrazines by the CuCl-catalyzed reaction of *tert*-butyl carbazates with arylboronic acids in the presence of air.[9] Buchwald reported the synthesis of *N*-aryl hydrazides by copper-catalyzed coupling of hydrazides with aryl iodides.[10]

SCHEME 1



The reaction of phenylboronic acid (1.0 mmol, **1a**) with di-*tert*-butyl azodicarboxylate (**2**, 0.5 mmol) in the presence of $[CuOTf]_2$·benzene (0.025 mmol) in toluene (1 mL) at room temperature for 20 h under N_2 gave phenylhydrazine derivative **3a** in 8% yield and Boc-NH-NHBoc **4** in 43% yield, along with recovery of **2** in 43% yield. The use of 1,2-dichloroethane as a solvent improved the yield of **3a** to 61%, along with 34% of **2**, and **4** was not formed. The use of THF dramatically increased the yield of **3a** to 90% yield with the complete consumption of **2**, and no **4** was formed. Although DMF gave a comparable yield (95%), THF was selected as the solvent of choice in this work because of its ease in handling. Copper catalysts were next examined. Several copper complexes showed catalytic activity: CuI (55%), CuCl (73%), $Cu(OTf)_2$ (86%), and $Cu(OAc)_2$ (88%). A rhodium complex $[Rh(OH)(cod)]_2$ was also found to function as a catalyst, although the yield and selectivity was low (**3a**: 22%, **4**: 44%). Based on these results, the standard reaction conditions employed were as follows: **1a** (1 mmol), **2** (0.5 mmol), $Cu(OAc)_2$ (0.05 mmol) in THF (1 mL) at room temperature for 20 h under N_2.



The reaction of various arylboronic acids **1** with **2** was carried out under standard reaction conditions and the results are shown in Table 1. It is noteworthy that the reaction was not significantly affected by the electronic nature of the functional groups present. However, the use of fluoro-substituted phenylboronic acids, as in **1g** and

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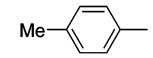
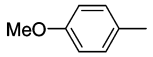
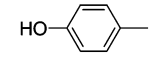
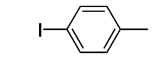
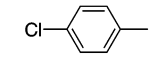
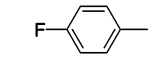
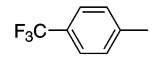
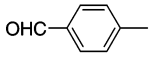
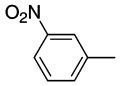
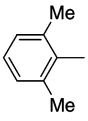
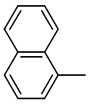
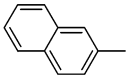
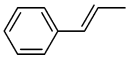
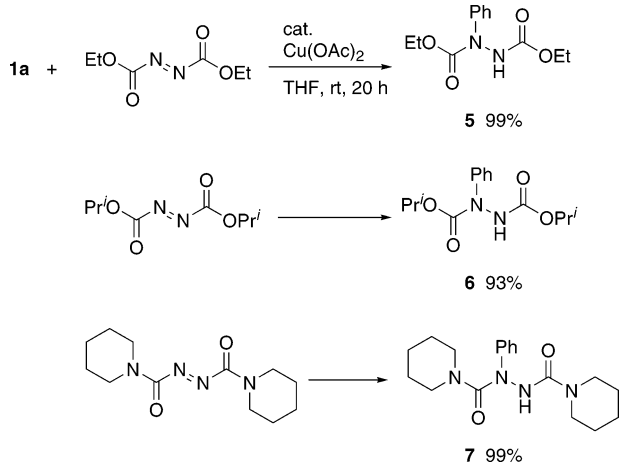
TABLE 1. Cu(OAc)$_2$-Catalyzed Reaction of Di-*tert*-butyl Azodicarboxylate (2) with Organoboronic Acids 1[a]

entry	Ar		yield
1		**a**	88%
2		**b**	96%
3		**c**	97%
4		**d**	96%
5		**e**	93%
6		**f**	93%
7		**g**	49%
8		**h**	13%
9		**i**	67%
10		**j**	98%
11		**k**	96%
12		**l**	<5%
13		**m**	<5%
14		**n**	99%
15		**o**	93%
16		**p**	99%
17		**q**	62%

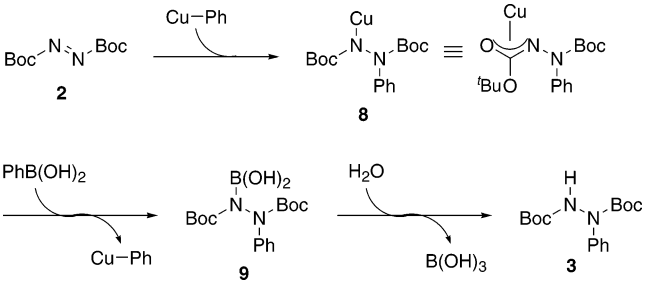
[a] Reaction conditions: **1** (1 mmol), **2** (0.5 mmol), and Cu(OAc)$_2$ (0.05 mmol) in THF (1 mL) at rt for 20 h under N_2.

1h, led to reduced yields of the corresponding hydrazines (entries 7 and 8). The presence of even an iodide or nitro group on the phenyl ring had no effect on the efficiency of the reaction (entries 5 and 10). In contrast to the

SCHEME 2



SCHEME 3. Proposed Reaction Mechansim



electronic nature of substituent groups, the reaction was significantly affected by steric factors. A reaction with 2,6-dimethylphenylboronic acid (**1l**) gave only a small amount (<5% yield) of the expected product **3l** (entry 12). The reaction of 2-methoxyphenylboronic acid (**1m**) also resulted in a poor yield (<5% yield) (entry 13). The reaction is not limited to a phenyl ring, but is also applicable to a naphthalene ring and heteroaromatic rings (entries 14−16). However, 3-pyridinylboronic acid did not give the corresponding hydradine. The reaction of styrylboronic acid gave the corresponding hydrazine **3q** in 62% yield (entry 17). An alkylboronic acid, such as butylboronic acid, was found to be unreactive.

The reaction was also applicable to other azodicarboxylate derivatives, as shown in Scheme 2. In all cases, the corresponding phenylhydrazines **5**−**7** were obtained in quantitative yields by the reaction of **1a**.

Organotin or silicon reagents have recently been shown to have a reactivity similar to organoboron reagents. For example, these organometallic reagents undergo conjugate additions to α,β-unsaturated carbonyl compounds.[11] The use of PhSnBu$_3$ in place of **1** under standard reaction conditions resulted in no reaction. However, the reaction took place to give **3a** in 17% yield when the reaction was carried out at 100 °C. PhSiMe$_3$ did not function as a phenylation reagent, even at 100 °C.

The proposed mechanism for this reaction is shown in Scheme 3. The reaction of Cu(OAc)$_2$ with PhB(OH)$_2$ gives a Ph-Cu species,[12] which adds to azodicarboxylate **2** to

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give **8**. The transmetalation of **8** with $PhB(OH)_2$ followed by protonolysis gives **3**. We anticipated that **4** would be an intermediate in the formation of **3a** because **4** was formed in some cases and the $Cu(OAc)_2$-catalyzed reaction of **4** with arylbismuth compounds has previously been reported.[8] It was, however, confirmed that **4** is not a primary intermediate in the formation of **3a** based on the results of the following experiments. The reaction of **4** with $PhB(OH)_2$ under standard reaction conditions (under N_2) resulted in no reaction, with **4** being recovered. In contrast, **3a** was formed in 40% yield when the reaction of **4** was carried out under standard reaction conditions, but in the presence of air. The *N*-arylation of amines using $PhB(OH)_2$ is known to proceed in the presence of a stoichiometric amount of a copper salt or in the presence of a catalytic amount of a copper salt with added oxidizing reagents present.[13] Since the present reaction was carried out under N_2, **4** is not an intermediate in the formation of **3**.

In summary, we demonstrated, with emphasis on scope and limitations, that aryl- or vinylboronic acids **1** add to the N=N double bond in diazodicarboxylates under mild reaction conditions with a high efficiency. This method is operationaly simple. The reaction is a useful method for the preparation of aryl-substituted hydrazines and tolerates a wide variety of functional groups. Aryl-substituted hydrazines can be easily converted to the corresponding anilines by reduction with zinc dust in acetic acid or Raney-Ni.[4a,4b,4e]

Experimental Section

Typical Procedures. To a stirred solution of phenyl boronic acid (1.0 mmol, **1a**) with di-*tert*-butyl azodicarboxylate (**2**, 0.5 mmol) in THF (1 mL), was added, in one portion, $Cu(OAc)_2$ (0.05 mmol, 9 mg). The mixture was stirred at room temperature for 20 h under N_2. After the removal of the solvent, the residue was purified by chromatography (silica gel, heaxane/EtOAc = 10/1) to give 1,2-bis(*tert*-butyloxycarbonyl)-1-phenylhydrazine (**3a**, 135 mg, 88%) as a white solid. Spectral data for compounds **3a**, **3b**, **3c**, **3f**, **3j**, **3k**, and **3p** have been reported previously.[9] Compounds **3n**[8b] and **5**[14] are also known compounds.

1,2-Bis(*tert*-butyloxycarbonyl)-1-(4-hydroxyphenyl)hydrazine (3d): white solid; mp 86−88 °C (1 mmHg); R_f 0.46 (hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 18H), 6.65 (d, J = 8.6 Hz, 2H), 6.88 (br s, 1H), 7.15 (d, J = 6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 28.2, 28.3, 81.6, 82.3, 115.4, 126.3, 134.2, 154.4, 154.6, 155.4; IR (KBr) 3371 m, 3035 w, 2979 m, 2935 w, 1699 s, 1612 w, 1599 w, 1516 s, 1477 w, 1458 m, 1394 m, 1369 s, 1267 m, 1254 s, 1101 w, 1059 w, 1030 w, 1009 w, 903 w, 839 w, 787 w, 762 w, 580 w, 413 w; MS *m/z* (relative intensity) 324 (M^+, 2), 168 (88), 123 (10), 57 (100). Anal. Calcd for $C_{16}H_{24}N_2O_5$: C, 59.24; H, 7.46; N, 8.64. Found: C, 58.87; H, 7.30; N, 8.60.

1,2-Bis(*tert*-butyloxycarbonyl)-1-(4-iodophenyl)hydrazine (3e): white solid; mp 169 °C (1 mmHg); R_f 0.17 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.49 (s, 18H), 6.40; 6.70 (br s, 1H), 7.19 (d, J = 7.6 Hz, 2H), 7.61 (d, J = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 28.2, 28.2, 81.8, 82.7, 89.4, 125.0, 137.2, 141.8, 153.0, 155.1; IR (KBr) 3342 m, 3001 w, 2981 m, 2935 w, 1736 s, 1724 s, 1709 s, 1496 s, 1454 w, 1394 m, 1369 s, 1317 m, 1277 m, 1254 s, 1215 w, 1161 s, 1061 m, 1003 w, 908 w, 856 w, 839 m, 827 w, 787 w, 756 w, 717 w, 519 w; MS *m/z* (relative intensity) 434 (M^+, 0.3), 278 (30), 57 (100). Anal. Calcd for $C_{16}H_{23}IN_2O_4$: C, 44.25; H, 5.34; N, 6.45. Found: C, 44.24; H, 5.17; N, 6.46.

1,2-Bis(*tert*-butyloxycarbonyl)-1-(4-fluorophenyl)hydrazine (3g): white solid; mp 131 °C (1 mmHg); R_f 0.23 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.49 (s, 18H), 6.46, 6.74 (br s, 1H), 7.00 (tt, J = 8.6 Hz, 2.0 Hz, 2H), 7.37 (br s, J = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 28.1, 28.2, 81.7, 82.4, 115.1 (d, J = 22.4 Hz), 125.9, 138.2, 153.7, 155.4, 160.4 (d, J = 245.3 Hz); IR (KBr) 3282 s, 2999 w, 2985 m, 2970 w, 2931 w, 1739 m, 1716 s, 1516 s, 1475 w, 1458 w, 1369 s, 1342 s, 1298 m, 1277 m, 1223 m, 1173 s, 1155 s, 1011 m, 904 w, 858 w, 839 m, 793 w, 760 w, 739 w, 671 w, 569 w, 525 w; MS *m/z* (relative intensity) 326 (M^+, 0.1), 170 (100), 126 (21), 109 (11), 59 (13), 57 (100). Anal. Calcd for $C_{16}H_{23}FN_2O_4$: C, 58.88; H, 7.10; N, 8.58. Found: C, 58.53; H, 6.97; N, 8.37.

1,2-Bis(*tert*-butyloxycarbonyl)-1-(4-trifluoromethylphenyl)hydrazine (3h): white solid; mp 125−127 °C (1 mmHg); R_f 0.23 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.51 (s, 18H), 6.64, 6.82 (br s, 1H), 7.56 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 28.1, 28.1, 82.1, 83.2, 122.3, 124.1 (q, J = 271.6 Hz), 125.6 (q, J = 3.9 Hz), 126.8 (q, J = 32.5 Hz), 145.0, 153.0, 155.3; IR (KBr) 3327 m, 3294 m, 2985 m, 2937 w, 1716 s, 1618 w, 1500 m, 1460 m, 1425 w, 1394 m, 1371 s, 1323 s, 1271 m, 1252 s, 1211 m, 1151 s, 1115 s, 1072 s, 1009 m, 901 w, 839 m, 789 w, 760 m, 688 w, 642 w, 594 w; MS *m/z* (relative intensity) 376 (M^+, 0.06), 220 (36), 57 (100). Anal. Calcd for $C_{17}H_{23}F_3N_2O_4$: C, 54.25; H, 6.16; N, 7.44. Found: C, 54.65; H, 6.14; N, 7.14.

1,2-Bis(*tert*-butyloxycarbonyl)-1-(4-formylphenyl)hydrazine (3i): white solid; mp 95−97 °C (1 mmHg); R_f 0.089 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.53 (s, 18H), 6.43; 7.06 (br s, 1H), 7.65 (d, J = 8.2 Hz, 2H), 7.82 (d, J = 8.2 Hz, 2H), 9.93 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 28.1, 28.1, 82.0, 83.2, 121.6, 130.1, 132.4, 147.2, 152.5, 155.0, 191.0; IR (KBr) 3290 m, 2981 m, 2933 m, 1736 s, 1701 s, 1604 m, 1579 m, 1510 m, 1479 m, 1458 m, 1394 m, 1369 s, 1302 s, 1252 s, 1151 s, 1055 m, 1007 m, 903 w, 850 m, 760 m, 625 w, 515 w; MS, *m/z* (relative intensity) 336 (M^+, 0.1), 180 (43), 136 (13), 57 (100). Anal. Calcd for $C_{17}H_{24}N_2O_5$: C, 60.70; H, 7.19; N, 8.33. Found: C, 60.31; H, 6.89; N, 8.27.

1,2-Bis(*tert*-butyloxycarbonyl)-1-(2,6-dimethylphenyl)-hydrazine (3l): MS *m/z* (relative intensity) 336 (M^+, 1.3), 180 (54), 119 (11), 57 (100).

1,2-Bis(*tert*-butyloxycarbonyl)-1-(2-methoxyphenyl)hydrazine (3m): MS *m/z* (relative intensity) 338 (M^+, 0.03), 182 (26), 71 (11), 57 (100).

1,2-Bis(*tert*-butyloxycarbonyl)-2-naphthylhydrazine (3o): white solid; mp 132−133 °C (1 mmHg); R_f 0.23 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.51, 1.52 (two s overlapped, 18H), 6.52, 6.83 (br s, 1H), 7.44 (t, J = 3.6 Hz, 2H), 7.57 (d, J = 7.3 Hz, 1H), 7.79 (d, J = 8.6 Hz, 3H), 7.85 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 28.2, 81.5, 82.3, 121.2, 122.8, 125.4, 126.0, 127.3, 127.8, 127.9, 131.2, 133.2, 139.5, 153.5, 155.2; IR (KBr) 3338 m, 3303 m, 3060 w, 2978 m, 2931 w, 1720 s, 1633 w, 1601 w, 1510 m, 1477 w, 1458 w, 1392 m, 1369 s, 1336 s, 1317 m, 1271 m, 1248 m, 1178 s, 1151 s, 1126 m, 1057 w, 949 w, 854 w, 750 m, 567 w; MS *m/z* (relative intensity) 358 (M^+, 0.3), 202 (39), 57 (100). Anal. Calcd for $C_{20}H_{26}N_2O_4$: C, 67.02; H, 7.31; N, 7.82. Found: C, 66.88; H, 7.17; N, 7.72.

1,2-Bis(*tert*-butyloxycarbonyl)-1-styrylhydrazine (3q): white solid; mp 127 °C (1 mmHg); R_f 0.29 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.49 (s, 18H), 6.07 (d, J = 14.2 Hz, 1H), 6.15; 6.36 (br s, 1H), 7.12 (d, J = 6.0 Hz, 1H), 7.20−7.41 (c, 4H), 7.62 (d, J = 14.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 28.1, 81.8, 82.7, 109.3, 125.5, 126.0, 126.9, 128.4, 136.3, 151.9, 153.6; IR (KBr) 3298 s, 3086 w, 3059 w, 3006 m, 2978 m, 2933 m, 1722 s, 1651 s, 1601 w, 1510 s, 1448 m, 1367 s, 1304 s, 1252 s, 1153 s, 1055 m, 1024 w, 960 w, 943 m, 866 m, 850 m, 785 w, 746 s, 698 m, 553 w, 517 w; MS *m/z* (relative intensity) 334 (M^+, 1.6), 178 (81), 117 (22),

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57 (10). Anal. Calcd for $C_{18}H_{26}N_2O_4$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.54; H, 7.81; N, 8.23.

1-Phenyl-1,2-bis(isopropoxycarbonyl)hydrazine (6): white solid; mp 90 °C (1 mmHg); R_f 0.11 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.28 (d, J = 5.9 Hz, 12H), 5.02 (qq, J = 6.3 Hz, 4.6 Hz, 2H), 6.64, 6.85 (br s, 1H), 7.19 (t, J = 7.3 Hz, 1H), 7.34 (t, J = 7.3 Hz, 2H), 7.43 (d, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.9, 22.0, 70.0, 70.8, 123.8, 125.8, 128.3, 141.6, 154.2, 155.9; IR (KBr) 3280 s, 3033 w, 2985 m, 2937 w, 1716 s, 1599 w, 1518 s, 1493 s, 1456 m, 1377 s, 1340 m, 1311 s, 1255 s, 1200 s, 1147 m, 1107 s, 1053 m, 1016 m, 876 w, 835 w, 777 m, 756 m, 706 s, 634 w, 517 w, 438 w; MS *m/z* (relative intensity) 280 (M^+, 1), 194 (16), 152 (100), 134 (11), 108 (19), 107 (65), 105 (12), 91 (14), 77 (25). Anal. Calcd for $C_{14}H_{20}N_2O_4$: C, 59.99; H, 7.19; N, 9.99. Found: C, 59.79; H, 6.94; N, 9.93.

1-Phenyl-1,2-bis(piperidinylcarbonyl)hydrazine (7): white solid; mp 60 °C (1 mmHg); R_f 0.11 (hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$) δ 1.51−1.61 (m, 12H), 3.34−3.45 (m, 8H), 7.07 (t, J = 7.3 Hz, 1H), 7.14 (d, J = 7.6 Hz, 2H), 7.29 (t, J = 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 24.3, 24.4, 25.2, 25.6, 45.1, 46.6, 120.7, 123.8, 128.8, 145.5, 157.6, 158.9; IR (KBr) 3265 m, 3030 w, 2935 s, 2854 s, 1649 s, 1597 s, 1531 s, 1491 s, 1466 s, 1441 s, 1429 s, 1412 s, 1254 s, 1230 s, 1146 m, 1022 m, 985 m, 953 w, 899 w, 870 w, 852 m, 820 w, 748 m, 694 m, 648 w, 615 m, 565 w; MS *m/z* (relative intensity) 330 (M^+, 0.4), 246 (13), 245 (80), 112 (100), 69 (54); Anal. Calcd for $C_{18}H_{28}N_4O_2$: C, 65.43; H, 7.93; N, 16.96. Found: C, 65.38; H, 7.71; N, 16.84.

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