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# Scope and Limitations of the Palladium-Catalyzed Cross-Coupling Reaction of in situ Generated Organoboranes with Aryl and Vinyl Halides

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**Abstract:**

*Summary:* The *in situ* palladium(0)-catalyzed Suzuki reaction is shown to be an efficient method for the cross-coupling of aryl-, furyl-, primary, and benzylic boranes with aryl or vinyl bromides and iodides without the isolation of the organoboronic acid or the addition of any external base.

**Tables:**

**Table 1. Various Attempts To Optimize the Yield of Biphenyl via the *in Situ* Suzuki Cross-Coupling Reaction**

| entry | solvent | PhX | water or base | catalyst | time (h) | yield[a] of biphenyl (%) |
|---|---|---|---|---|---|---|
| 1 | DME | I | $Na_2CO_3$ | $Pd(PPh_3)_4$ | 20 | 68 |
| 2 | DME | I | $Na_2CO_3$ | $Pd(PPh_3)_4$ | 2 | 53 |
| 3[b] | benzene | I | $Na_2CO_3$ | $Pd(PPh_3)_4$ | 16 | 61[c] |
| 4[b] | benzene | I | $H_2O$ | $Pd(PPh_3)_4$ | 16 | 51[d] |
| 5[b] | benzene | I | $Na_2CO_3$ | $Pd(OAc)_2(PPh_3)_2$ | 20 | 85 |
| 6 | NMP | Br | $H_2O$ | $Pd(PPh_3)_4$ | 17 | 63 |
| 7 | DME | Br | $H_2O$ | $Pd(PPh_3)_4$ | 1.5 | 62 |
| 8 | DME | Br | $H_2O$/TMEDA[e] | $Pd(PPh_3)_4$ | 1.5 | 59 |
| 9 | DME | Br | $Na_2CO_3$ | $Pd(OAc)_2(PPh_3)_2$ | 2 | 76 |
| 10 | DME | Br | $Na_2CO_3$ | $Pd(PPh_3)_4$ | 2 | 49 |
| 11 | DME | Br | $Na_2CO_3$ | $Pd(Pfuryl_3)_4$ | 5 | 53 |
| 12 | DME | Br | $H_2O$ | $Pd(Ph_3)_4$ | 1.5 | 59 |
| 13 | DME | Br | none | $Pd(Ph_3)_4$ | 2 | 9 |
| 14[f] | DME | Br | $H_2O$ | $Pd(Ph_3)_4$ | 1.75 | 21 |

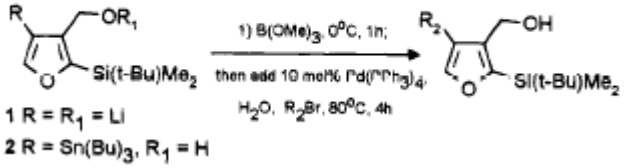
[a] Yield obtained by distillation and NMR analysis of the distillate. [b] Aryllithium generated by halogen−metal change of iodobenzene in ether at −95 °C for 10 min. [c] 16% yield of butylbenzene. [d] 12% yield of butylbenzene. [e] 1.0 equiv of TMEDA was added. [f] Boronic acid prepared from phenylmagnesium chloride.

**Table 2. Cross Coupling of *in Situ* Generated Organoboranes with Organo Halides**

| entry | halide | boronic acid source | catalyst | solvent | water source | time (h) | product (% yield) |
|---|---|---|---|---|---|---|---|
| 1 | bromobenzene | **5** | $Pd(PPh_3)_4$ | benzene | $H_2O$ | 15 | **10** (55) |
| 2 | iodobenzene | iodobenzene | $Pd(PPh_3)_4$ | benzene | 2 M $Na_2CO_3$ | 20 | biphenyl (85) |
| 3 | bromobenzene | *n*-BuLi | $Pd(OAc)_2(PPh_3)_2$ | THF | $H_2O$ | 20 | *n*-butylbenzene (52) |
| 4 | 2-bromobenzaldehyde | benzyllithium | $Pd(PPh_3)_4$ | toluene | 2 M $Na_2CO_3$ | 20 | 2-benzylbenzaldehyde (83) |
| 5 | bromobenzene | **6** | $Pd(PPh_3)_4$ | benzene | 2 M $Na_2CO_3$ | 16 | **11** (95) |
| 6 | bromobenzene | **7** | $Pd(PPh_3)_4$ | THF | $H_2O$ | 48 | **12** (39) |
| 7 | bromobenzene | *s*-BuLi | $Pd(OAc)_2(PPh_3)_2$ | benzene | $H_2O$ | 16 | mixture (<30) |
| 8 | **3** | **8** | $Pd(PPh_3)_4$ | THF | $H_2O$ | 19 | **13** (43) |
| 9 | **4** | **9** | $Pd(PPh_3)_4$ | DME | $H_2O$ | 2 | **14** (72) |

**Schemes:**

**Scheme 1**




**1** R = $R_1$ = Li

**2** R = Sn(Bu)$_3$, $R_1$ = H

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