

Pd(0)-Catalyzed Ortho-Ortho Coupling Reaction

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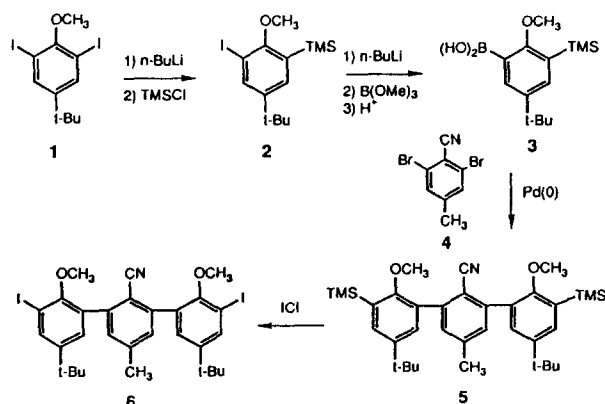
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Among the many known aryl-aryl coupling reactions,¹ the palladium(0)-catalyzed Suzuki reaction has become the most popular.² A major advantage of this reaction is that it is compatible with many functional groups such as hydroxyl, nitrile, nitro, trimethylsilyl (TMS), aldehyde, ketone, ester, amide, and alkenyl. Furthermore this reaction is relatively easy to perform, because it does not require the anhydrous conditions which are crucial for other reactions. On the other hand this reaction is relatively slow³ and quite sensitive to steric hindrance.⁴

The sensitivity of this reaction to ortho substituents has not been carefully scrutinized. Snieckus and coworkers have demonstrated that this reaction may be conducted in the presence of an ortho carboxamide group.⁵ In this communication the sensitivity of this reaction to a variety of ortho substituents is reported.

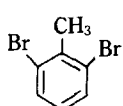
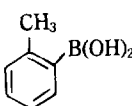
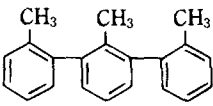
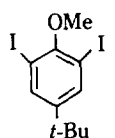
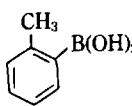
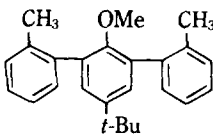
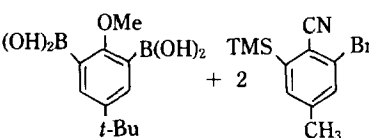
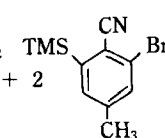
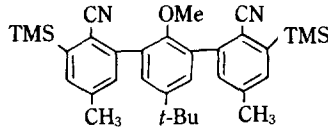
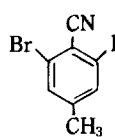
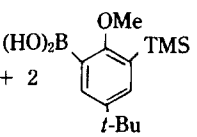
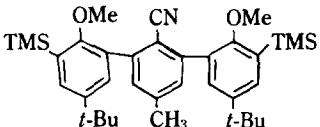
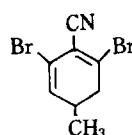
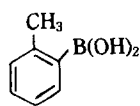
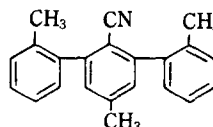
The results are summarized in Table 1. The reaction is very tolerant of ortho-methyl (entries 1 and 2) and methoxyl groups (entries 2-4), whether these substituents are in the



Scheme 1

boronic acid or the halide coupling partner. In this study, when the methoxyl group was in the halide coupling partner, the halogen atom was always iodine. Good yields were obtained with an ortho nitrile functional group, provided that it was in the halide coupling partner (entries 3-5). When the nitrile functional group was in the boronic acid coupling partner, very poor results were obtained (entries 15-18). Perhaps the nitrile functional group activates the B(OH)₂ group towards protodeboronation (many heterocyclic boronic acids are hydrolytically unstable). The results shown in entries 6-13 demonstrate the usefulness of this reaction for the formation of terphenyls and quarterphenyls containing tertiary benzamide functional groups. An ortho tertiary benzamide func-

Table 1. The Results of Pd(0) Catalyzed ortho-ortho Aryl-Aryl Coupling Reactions

#	Starting materials	Product	Yield (%) ^a	Remarks
1	 + 2 		75.0	^b
2	 + 2 		86.0	^b
3	 + 2 		76.6	^b
4	 + 2 		79.7	^b
5	 + 2 		33.7	^b

6		55.0	^b
7		61.0	^b
8		0.0	^b
9		40.2	^b
10		40.8	^b
11		10.0	^c
12		30.0	^c
13		35.0	^b
14		0.0	^b
15		0.0	^b
16		0.0	^b
17		0.0	^b
18		0.0	^b

^a Isolated yield, but not optimized, ^b Heterogeneous condition (EtOH/Benzene/2 N Na₂CO₃), ^c Homogeneous condition (Toluene/N,N-dimethylacetamide/anhydrous K₂CO₃).

nal group is well-tolerated in the boronic acid coupling partner (entries 6, 9, 10, 12). It is also well-tolerated in the halide coupling partner provided that the halogen atom is iodine (entries 7, 9, 10, 12). This coupling reaction could even be performed when both the boronic acid and the iodide coupling partners contain ortho tertiary benzamide groups (entries 9, 10, 11, 12). In this latter type of coupling, slightly lower yields were observed for the formation of quarterphenyls as compared to terphenyls. This is probably due to a buildup of steric congestion in these highly substituted oligomers.

The trimethylsilyl (TMS) group was successfully used as a protecting group for bromide or iodide owing to the stability of the TMS group under the Suzuki reaction conditions (entries 3, 4) and the ease with which aryl silanes undergo desilylation with bromine or iodine monochloride.⁶ An example is shown in Scheme 1. Aryl diiodide **1** was mono-protected with a TMS group (**2**), and then transformed to boronic acid **3** in one pot. Boronic acid **3** was coupled with aryl dibromide **4** to give terphenyl **5** (entry 4) in 79.9% yield. Finally **5** was transformed to **6** by iododesilylation.

The representative heterogeneous coupling reaction for terphenyl **5** was performed as follows; Dibromide **4** (1.38 g, 5 mmol) and tetrakis (triphenylphosphine) palladium(0) (8.9 mg, 0.08 mol%) were dissolved in 20 ml of toluene. Boronic acid **3** (3.38 g, 12 mmol), 2 M sodium carbonate solution (10 ml), and ethyl alcohol (10 ml) were added. The mixture was refluxed for 24 hours and cooled to room temperature. The organic phase was separated and the aqueous phase was extracted with 20 ml of ether twice. The combined organic phases were dried with brine and then with anhydrous magnesium sulfate. The solvent was evaporated, and the crude mixture was purified by column chromatography (4×30 cm, dichloromethane/hexane=1/1). The pure product **5** was obtained in 79.7% yield (2.33 g) after crystallization from a mixture of dichloromethane and hexane.

In conclusion, good yields were usually obtained in Suzuki aryl-aryl coupling reactions, even when both coupling partners had a sterically hindered ortho substituent such as tertiary amide group.

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Roles of EDTA in Silver Sol-Fourier Transform Raman Spectroscopic Study Using Nd:YAG cw 1064 nm Excitation

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The silver colloidal suspension prepared by reduction of AgNO₃ with EDTA¹ has been used for surface-enhanced Raman scattering effects and surface adsorption behaviors of adsorbates. The silver colloids prepared with EDTA reduction procedures are significantly stable for additives, *e.g.*, acids, bases or adsorbates compared to colloids reduced with NaBH₄² or citrate³. It was reported⁴ that they were stable for several hours even under pH=4 condition. The intense yellow-brownish color developed during sol preparation with EDTA exhibited an absorption maximum at 414 nm. When colloids become aggregated to the larger size, they can turn color and develop another absorption band near the higher wavelength (in the range 500-700 nm). This requires understanding of the colloidal particle size. The average particle size of aqueous silver colloids determined by employing the proton correlation spectroscopy was about 20 nm in diameter⁵. The particle size was not much affected with time nor after addition of additives, such as pyridine, within experimental errors.

The excitation by cw 1064 nm of Nd:YAG laser has several advantages to the shorter wavelength excitation, *e.g.*, photodecomposition of photolabile compounds⁶, non-resonant condition of chromophores^{7,8}, etc.. The excitation using 1064 nm is sufficiently far from surface plasmon absorption, from colloids absorption, or from the absorption of the possible charge-transfer complex between metal surface and adsorbates. Therefore this technique can provide well-defined non-resonant surface enhanced Raman spectra of adsorbed chromophores⁷ of superior quality using Fourier transform advantages, coadding and multiplexing capabilities.⁹ In this paper Fourier transform (FT) Raman spectroscopy using cw 1064 nm excitation is applied to elucidate the roles of EDTA which survived during silver sol preparation for the stability of EDTA-reduced silver colloids.

Figure 1 illustrates FT-Raman spectra of EDTA and EDTA-Ag⁺ ion complex in various states between 800 and 1800 cm⁻¹. Figure 1(a) and 1(b) shows FT-Raman spectrum of disodium EDTA salt and tetrasodium EDTA salt in powder state, respectively. At a glance of above two spectra, the spectrum of tetrasodium EDTA is much simpler than that of disodium EDTA. It can mean better symmetry in the structure of tetraanion EDTA⁴⁻. Two bands at 899 and 916 cm⁻¹ in Figure 1(a) collapse into one broad band at 913 cm⁻¹ in Figure 1(b). This band at 913 cm⁻¹ is due primarily to the C-C stretching mode of C-CO₂⁻ moiety of tetraanion EDTA. Splitting into two in the spectrum of dianion EDTA would indicate the nonequivalence of two C-C stretching modes between C-CO₂H and C-CO₂⁻ moieties of disodium EDTA. Therefore two bands at 899 and 916 cm⁻¹ in