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## Symmetric diarylacetylenes: one-pot syntheses and solution photoluminescence

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#### ABSTRACT

Bis(tri-*n*-butylstannyl)acetylene was synthesized and used to create a series of symmetric diarylacetylenes via a one-step Stille coupling protocol with  $Pd(PPh_3)_4$  as the catalyst. In many cases, the product simply crystallized in good yields from the reaction mixture upon cooling after reflux at 100 °C or upon removal of solvent. The diarylacetylenes were studied using UV-vis and fluorescence spectroscopies, which showed that naphthyl- and biphenyl-substituted acetylenes had very high solution-state fluorescence quantum yields.

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Carbon–carbon bond formation through palladium catalysis is a useful tool in the organic chemistry toolbox.<sup>1</sup> Palladium–catalyzed organotin Stille coupling<sup>2</sup> offers gentle reaction conditions and good yields. Diarylacetylenes are of interest in the fields of natural products<sup>3</sup> and materials science,<sup>4</sup> especially in the field of electronic materials because of extended conjugation between the aryl groups through the acetylene. In this investigation, a versatile, one-pot Stille coupling method is used to create symmetric diarylacetylenes. This work describes facile work-up procedures en route to the isolation of a series of  $\pi$ -conjugated diaryl-substituted acetylenes and the investigation of the relationship between the diaryl-acetylene structures and their solution-state absorbance and optoelectronic properties.

A traditional synthesis of a symmetric diarylacetylene involves Sonogashira coupling, completed in three steps.<sup>5</sup> The first involves coupling an aryl halide to trimethylsilylacetylene using a palladium catalyst (Scheme 1), followed by desilylation, and a second Sonogashira coupling of the aryl halide. A recent study by Hua and co-workers described a similar one-pot, three-step synthesis of diarylacetylenes starting from 2-methyl-3-butyn-2-ol.<sup>6</sup> Another method to make symmetric diarylacetylenes utilizes acetylene gas under Sonogashira conditions in one step, although the aryl halides were limited to aryl iodides, *E*-2-bromostyrene, and bromopyridine.<sup>5a,7</sup> More recently, Therien and co-workers described a onestep diaryl addition to a diboronate-substituted acetylene under Suzuki–Miyaura conditions.<sup>8</sup>

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Scheme 1. Synthesis of diarylacetylenes using Sonogashira method.

Stille et al.,<sup>9a</sup> first showed that the three steps of the Sonogashira protocol could be combined into a one-step reaction involving bis(tri-*n*-butylstannyl)acetylene (1), an aryl iodide and a palladium catalyst (CH<sub>3</sub>CN)<sub>2</sub>PdCl<sub>2</sub>. This opened investigations into the utility of **1** as a reagent for the synthesis of other symmetric diarylacetylenes.9 Cummins9b demonstrated that a less expensive catalyst, Pd(PPh<sub>3</sub>)<sub>4</sub>, could be used to synthesize two bis(anisolyl)acetylenes and a bis(benzoyloxyphenyl)-acetylene as precursors to bis(hydroxyphenyl)alkynes. The Pd-catalysis reaction is tolerant of numerous functional groups and has been used in the synthesis of acetylenes containing ferrocenyl-type transition metal complexes,9a as well as organic functional groups such as esters9b and amides.<sup>9c</sup> Compound 1<sup>10</sup> has been used extensively as a reagent for the synthesis of a number of symmetric diarylacetylenes, but rarely has there been more than one compound synthesized per investigation and a systematic study of this coupling reaction is desired. In this study, we expand the scope of the previously reported Stille cross-coupling reaction with 1 to include a number of functionalities on the aryl halide precursors.

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Using palladium catalysis, we found that **1** was a useful starting material in synthesizing a library of diarylacetylenes in one-step reactions. Although it is commercially available, **1** is moderately expensive and, therefore, does not lend itself to large scale syntheses. We sought an inexpensive, large scale synthetic route to compound **1**. Jones and Lappert<sup>11</sup> first described the synthesis of **1** from acetylene gas. We used a modified method by Barton et al.,<sup>12</sup> to affordably synthesize **1**. Trichloroethylene was treated with *n*-butyllithium to create an intermediate dilithioacetylene, and compound **1** was produced by reaction of the dilithioacetylene with tri-*n*-butylstannyl chloride (Scheme 2). The product was isolated by vacuum fractional distillation in 70–90% yield, routinely in 50 g batches, with the main by-product being the lower boiling monosubstituted tin acetylene (Bu<sub>3</sub>SnC=CH).

The diarylacetylenes were synthesized utilizing Stille coupling palladium-catalysis (Eq. 1). Two equivalents of the aryl halide



**Scheme 2.** Synthesis of bis(tri-*n*-butylstannyl)acetylene.

Table 1						
Solution	photophysical	data i	for diar	ylacety	lene 2-14	

$$2 \operatorname{Ar-X} \xrightarrow{1, \operatorname{Pd}(\operatorname{PPh}_{3})_{4}, p - \operatorname{dioxane}}_{100 \ ^{\circ}\mathrm{C}, 2-6 \ h} \xrightarrow{Ar}_{2 \ \operatorname{Bu}_{3}\mathrm{Sn-X}}^{+} (1)$$

$$X = \operatorname{Br} I$$

were heated to 100 °C with 1 and 1–2 mol % Pd(PPh<sub>3</sub>)<sub>4</sub> for 1–6 h. All reactions were monitored by GC-MS and gave air- and room-temperature-stable diarylacetylenes 2-14 in yields from 37% to 96% (Table 1). In general, reactions at 100 °C with aryl iodides were complete in 1 h, whereas most reactions with aryl bromides required at least 2 h. The only reactants studied that did not yield acetylenes were chlorobenzene, 1-bromo-2,4,6-trimethylbenzene (bromomesitylene) and bromopentafluorobenzene, even after heating at 100 °C in *p*-dioxane for 6 h. Aryl chlorides are less reactive than their bromo and iodo counterparts<sup>2</sup> and this result is not unexpected. The mesityl substituent is sterically hindered at the ortho-positions, thus preventing the addition to the acetylene. In the case of bromopentafluorobenzene, the electronegative fluorines on the bromobenzene most likely reduce the reactivity toward Stille coupling reactions. although the fluorine atoms in the 2- and 6-positions are more sterically hindered than the hydrogens in other reactions.

A major benefit of this general procedure is that many of the reaction mixtures gave solid, even crystalline products upon cooling of the reaction mixture or upon evaporation of the *p*-dioxane. The solids could then be rinsed with hexanes to remove the liquid tin by-product, Bu<sub>3</sub>SnX (X = Br, I), and subsequently recrystallized from toluene or  $CH_2Cl_2$ /hexanes. Nitrogen-containing acetylenes could be easily separated from the tin by-product by acidification,

Compound	Ar	Х	Yield <sup>a</sup> (%)	$\lambda_{\max}^{b}$ (nm, abs)	$\lambda_{\max}^{c}$ (nm, em)	$arPhi^{d}$
2	<u> </u>	Cl, Br, I	X=Cl, 0X=Br, 37X=I, 80	299	369	0.007
3	N N	Br	96	-	372	0.016
4	N	Br	68	303	370	0.027
5	n-Bu}	Br	78	308	359, 377	0.061
6	Me <sub>3</sub> Si	Br	49	313	358, 378	0.161
7	Br→	I	82	313	357, 373	0.029
8	NC	Br	74	303, 324	362	0.369
9		Br	60	_	360, 377	0.708
10	Me <sub>3</sub> Si	Br	64	-	367, 386	0.764
11		Br	87	337, 359	368, 387	0.928
12		Br	77	317, 338	350, 368	0.846
13		Br	45	347, 364	375, 393	0.370
14	N=>ŧ	Br	76	321, 335, 349	357, 373	0.119

<sup>a</sup> Isolated yields.

<sup>b</sup> Measured in toluene (7.7  $\times$  10<sup>-6</sup> M).

<sup>c</sup> Measured in toluene ( $7.7 \times 10^{-6}$  M) and were excited at 330 nm.

<sup>d</sup> Determined with quinine sulfate  $(1.0 \times 10^{-5} \text{ M in H}_2\text{SO}_4)$ .<sup>15</sup>

separation and basicification. If the product did not solidify upon removal of solvent, the reaction mixture was taken up in diethyl ether and washed with saturated KF(aq), which turned the soluble tin bromide or iodide into the insoluble tri-*n*-butyltin fluoride that could be filtered away. As a last resort to separate the acetylene from the tin by-product, it was passed through silica gel, although this was only necessary for the very soluble compounds **2** and **5**.

Attempts were made to make bis(4-bromophenyl)acetylene, 7,<sup>4a-d</sup> a potentially useful starting material for other materials because the bromoaryl moiety is amenable to many further reactions. Initial attempts to make 7 from 1,4-dibromobenzene resulted in a mixture consisting of unreacted 1,4-dibromobenzene, bis(4bromophenyl)acetylene, bis(4-bromophenylethynyl)benzene, and insoluble phenylethynylene oligomers. When the starting material was switched to 1-bromo-4-iodobenzene and the reaction temperature was greater than 80 °C, 7 was efficiently synthesized at 82% isolated yield, with no evidence of coupling to produce larger phenylethynylenes. This result illustrates the reactivity difference between aryl bromides and iodides.

The optoelectronic properties of diarylacetylenes are of interest because of the  $\pi$ -conjugation resulting from their structures<sup>13</sup> and their optoelectronic properties are of interest to researchers in the fields of organic light-emitting diodes and fluorescent sensors. To the best of our knowledge, very few systematic investigations of diarylacetylenes have compared structure to optoelectronic properties.<sup>14</sup> The diarylacetylenes absorb and emit primarily in the ultraviolet region, so our focus was not only to determine which substituents gave red-shifted emissions, but also to observe which ones had the highest quantum yields in solution photoluminescence. The solution absorbance and photoluminescence properties of the compounds synthesized in this study are summarized in Table 1. For this discussion, 'one-ring' aromatic systems represent acetylenes with only one aryl ring (2-8) on either side of the acetylene triple bond such as pyridyl, 4-trimethylsilylphenyl, etc., and 'two-ring' aromatic systems represent those with two aryl rings (9–14) such as naphthyl, guinolinyl, etc.

The apparent first trend in reviewing the UV–vis data is that the one-ring acetylenes absorb light at shorter wavelengths than the two-ring acetylenes. The one exception is the cyano-substituted **8**, which showed two clear absorption maxima, whereas the others only exhibited one (or none >295 nm, in the case of **3**). The biphe-nyl-substituted **9** and **10** showed no maxima, although they absorbed out to approximately 370 nm. The other two-ring acetylenes showed two or three absorbtion maxima. The absorption by the two-ring acetylenes also tailed to longer wavelengths than by the one-ring acetylenes.

The diarylacetylene solutions were excited with 330 nm light,<sup>15</sup> which results in a visible purple glow in all solutions. It should be noted that the parent compound, diphenylacetylene (**2**), has the lowest quantum yield of any acetylene studied. Most acetylenes exhibited two emission bands in their spectra. The cyano-substituted **8** was unique among the one-ring acetylenes in that its solution-state photoluminescence quantum yield ( $\Phi_{PL} = 0.369$ ) was considerably larger than the next largest quantum yield one-ring acetylene (**6**,  $\Phi_{PL} = 0.161$ ). This result is expected when the UV-vis spectrum is considered because it has the highest intensity absorption of any of the one-ring acetylene at 330 nm. Compound **8** is also the only one-ring acetylene with  $\pi$ -electron density extended past the phenyl ring, which may explain why it absorbs at the longest wavelength.

Addition of a trimethylsilyl group in the 4-position of the phenyl ring (**6**) red-shifts the absorption and emission wavelength maxima by 9 nm from the parent diphenylacetylene (**2**). This red-shift of 9 nm also occurs in the emission spectrum of the unsubstituted bis(4-biphenyl)acetylene **9** upon addition of a trimethylsilyl group to the 4'-position of the biphenyl ring (**10**). Quantum yields increase in both cases of adding a para-trimethylsilvl group to the parent phenyl- or biphenyl-substituted acetylenes. The biphenyl derivatives 9 and 10 have quantum yields of  $\Phi_{\rm PL}$  = 0.708 and 0.764, respectively. These are significantly larger than the analogous one-ring compounds 2 and 6, and most likely are a result of extended  $\pi$ -conjugation. Compound **11** had the highest quantum yield ( $\Phi_{PL}$  = 0.928) emission and was the most red-shifted of the strong emitters. This large quantum yield was similar to that of compound **12** ( $\Phi_{PL}$  = 0.846), but by shifting the acetylene from the 1- to the 2-position on the naphthyl ring, the emission  $\lambda_{max}$  decreases by 19 nm. Due to the high quantum yields, 11 and 12 are attractive precursor targets for optoelectronic devices. Upon adding a nitrogen to the naphthylenyl moiety to create quinolinyl-substituted acetylenes 13 and 14, the quantum yields decrease significantly ( $\Phi_{PL}$  = 0.370 and  $\Phi_{PL}$  = 0.119, respectively), although **13** has the longest wavelength emission  $\lambda_{max}$  of any acetvlene studied here. The quantum yield is higher for the 1substituted quinolinyl derivative than it is for the 2-substituted derivative, as it is for the naphthylenyl-substituted derivatives.

In summary, synthesis of compound **1** was described and it was shown to be a useful reagent in the synthesis of a variety of symmetric diarylacetylenes in moderate to high yields using a one-step Pd-catalysis reaction from aryl bromides and iodides. Crystallization from the reaction mixture in many cases makes this an attractive synthetic protocol. Solution-state emission spectra of the acetylenes show trends in intensity and wavelengths that may be exploited in future design for optoelectronic materials. The quantum yields of the 1-naphthyl, 2-naphthyl, 4-biphenyl, and 4'-trimethylsilyl-4-biphenyl substituted acetylenes were very high ( $\Phi_{PL} > 0.7$ ), which may be of use to investigators in the field of organic light-emitting diodes or fluorescent sensing.

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#### Supplementary data

Supplementary data (experimental procedures, spectroscopic data for all new compounds, UV–vis absorption and fluorescence spectra in toluene) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.02.062.

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