

# Palladium-Catalyzed Annulation of *o*-Iodobiphenyls with *o*-Bromobenzyl Alcohols: Synthesis of Functionalized Triphenylenes via C–C and C–H Bond Cleavages

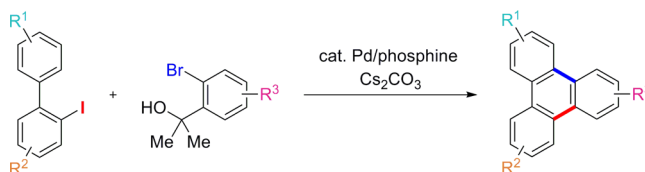
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## ABSTRACT



Treatment of *o*-iodobiphenyls with *o*-bromobenzyl alcohols in the presence of cesium carbonate under palladium catalysis affords a series of highly substituted triphenylenes. The reaction involves two C–C bond formations and C–C and C–H bond cleavages. A combination of palladium and an electron-deficient phosphine ligand proves to be effective for both decarbonylative cross-coupling and intramolecular cyclization.

Polycyclic aromatic hydrocarbons (PAHs) are regarded as one of the most important groups of compounds in

materials science due to their unique electronic and photo-physical properties.<sup>1</sup> Among them, triphenylenes have garnered much interest and have been used to construct functional organic materials such as discotic liquid crystals<sup>2,3</sup> and organic light-emitting diodes.<sup>4</sup> However, the construction of the triphenylene skeletons is challenging because the C–C bonds linking the benzene rings have to be constructed one by one.<sup>5</sup> To date, the standard synthetic method for the preparation of triphenylenes has been the

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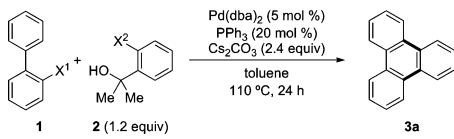
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cyclization of *o*-terphenyls under severe acidic and/or oxidative conditions.<sup>6</sup> However, since many functional groups cannot tolerate such harsh reaction conditions, the scope of this triphenylene synthesis is limited. More recently, transition-metal catalyst-based approaches have attracted much attention as they offer synthetic routes that are highly efficient and compatible with various functional groups.<sup>7,8</sup> Nomura and Miura have reported two examples of substituted triphenylenes via the palladium-catalyzed annulation of *o*-dibromobenzenes with *o*-phenylbenzyl alcohols.<sup>9</sup> Larock also reported the synthesis of substituted triphenylenes by the palladium-catalyzed annulation of *o*-iodobiphenyls with in situ generated arynes.<sup>10</sup> These methods have the potential to significantly expand the substrate scope, but drawbacks remain: (1) the reaction with arynes lacks regioselectivity and as a result gives rise to a mixture of regioisomers; and (2) the starting substrates are often difficult to prepare. Herein, we report the synthesis of highly functionalized triphenylenes, including previously inaccessible unsymmetrical triphenylenes. These syntheses proceed via palladium-catalyzed annulation of *o*-iodobiphenyls with *o*-bromobenzyl alcohols which are readily prepared and also air- and moisture-stable. The reaction involves the decarbonylative cross-coupling of aryl iodides with tertiary benzylic alcohols and the subsequent intramolecular cyclization catalyzed by a palladium/phosphine complex.<sup>11</sup>

We initially investigated the effect of halides in the annulation of *o*-halobiphenyls **1** with *o*-halobenzyl alcohols **2** (Table 1).<sup>12</sup> When the reaction was conducted with *o*-bromobiphenyl (**1a**) and *o*-bromobenzyl alcohol **2a**, the desired triphenylene (**3a**) was obtained in 15% yield

(entry 1). However, the yields of **3a** further decreased when the corresponding chloride **2b** and iodide **2c** were used in place of **2a** (entries 2 and 3). The use of aryl triflate **1b** or aryl chloride **1c** in the reaction with **2a** gave no product **3a** at all (entries 4 and 5). Of the systems screened the combination of *o*-iodobiphenyl (**1d**) and *o*-bromobenzyl alcohol **2a** proved to be the best (entry 6).

**Table 1.** Effect of Halide in Palladium-Catalyzed Annulation Reaction of **1** with **2**<sup>a</sup>



entry	X <sup>1</sup>	X <sup>2</sup>	yield (%) <sup>b</sup>
1	Br ( <b>1a</b> )	Br ( <b>2a</b> )	15
2	Br ( <b>1a</b> )	Cl ( <b>2b</b> )	<1
3	Br ( <b>1a</b> )	I ( <b>2c</b> )	2
4	OTf ( <b>1b</b> )	Br ( <b>2a</b> )	0
5	Cl ( <b>1c</b> )	Br ( <b>2a</b> )	0
6	I ( <b>1d</b> )	Br ( <b>2a</b> )	26

<sup>a</sup> Conditions: **1** (0.25 mmol), **2** (0.3 mmol), Pd(dba)<sub>2</sub> (0.0125 mmol), PPh<sub>3</sub> (0.05 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (0.6 mmol) in toluene (1 mL). <sup>b</sup> Determined by the <sup>1</sup>H NMR analysis of the crude mixture using bromoform as an internal standard.

Various palladium/phosphine combinations were then screened as the potential catalysts using the best substrate combination (Table 1, entry 6), and the results are summarized in Table 2. Electron-deficient triarylphosphines gave better results than electron-rich phosphines, suggesting an accelerated C–H metalation process (entries 1–3). Similar trends have been observed in other palladium-catalyzed C–H functionalization reactions.<sup>13</sup> Trialkylphosphines such as PCy<sub>3</sub> (Cy = cyclohexyl) or P<sup>*t*</sup>Bu<sub>3</sub>, triphenylphosphite P(OPh)<sub>3</sub>, and bidentate ligands such as DPPE (1,2-bis(diphenylphosphino)ethane) or DPPF (1,1'-bis(diphenylphosphino)ferrocene) were much less active. The best ratio of palladium to ligand was 1 to 2, although at the lower end of this range precipitation of a palladium black was observed (entry 4). In the presence of Pd(II) precursors such as Pd(OAc)<sub>2</sub>, PdCl<sub>2</sub>, or PdCl<sub>2</sub>(NCMe)<sub>2</sub>, the reaction proceeded well (entries 5–7). Finally, PdCl<sub>2</sub>(NCPH)<sub>2</sub> provided **3a** in 81% yield (entry 8). In the case that the product **3a** was obtained in low yield, the intermediate **4a** and the homocoupled product **5**<sup>11a</sup> were detected by the <sup>1</sup>H NMR and GC-MS analyses. We confirmed that the reaction of the isolated **4a** proceeded under the optimized conditions to afford **3a** quantitatively.

A plausible mechanism is shown in Scheme 1, based on the detected intermediate, 2-bromo-*o*-terphenyl (**4a**). Oxidative addition of *o*-iodobiphenyl (**1d**) occurs to give an

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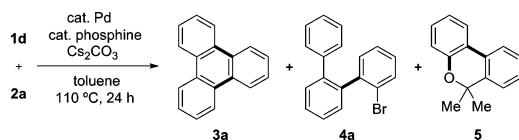
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(12) It is of note that the annulating reagents *o*-halobenzyl alcohols **2** actually need only a single step to prepare. Commercially available *o*-halobenzoate esters were treated with Grignard reagents to yield tertiary benzylic alcohols **2** quantitatively. When a methyl group was installed as a substituent at the benzylic position of **2**, the palladium-catalyzed decarbonylative coupling reaction yielded a stoichiometric amount of acetone, which is easily separable from the target triphenylene **3**.

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**Table 2.** Palladium-Catalyzed Annulation of *o*-Iodobiphenyl (**1d**) with *o*-Bromobenzyl Alcohol **2a**<sup>a</sup>



entry	Pd	phosphine	yield (%) <sup>b</sup>			
			3a	1d	4a	5
1	Pd(dba) <sub>2</sub>	PPh <sub>3</sub>	44	26	0	0
2		P(4-MeOC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	35	42	0	0
3		P[3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ] <sub>3</sub>	47	0	0	19
4 <sup>c</sup>			51	0	0	20
5	Pd(OAc) <sub>2</sub>		45	0	10	17
6	PdCl <sub>2</sub>		51	0	3	17
7	PdCl <sub>2</sub> (NCMe) <sub>2</sub>		51	0	0	23
8	PdCl <sub>2</sub> (NPh) <sub>2</sub>		81	0	4	16

<sup>a</sup> Conditions: **1d** (0.25 mmol), **2a** (0.3 mmol), a Pd source (0.0125 mmol), phosphine ligand (0.05 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (0.6 mmol) in toluene (1 mL). <sup>b</sup> Determined by GC analysis of the crude mixture using hexadecane as an internal standard. <sup>c</sup> P[3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>3</sub> (0.025 mmol) was used.

arylpalladium iodide **A**, at a rate faster than that with *o*-bromobenzyl alcohol **2a**. Base-assisted alkoxide–iodide exchange between **A** and **2a** then yields an aryl(alkoxy)palladium **B**. The sequential  $\beta$ -carbon elimination delivers a diarylpalladium complex **C** with a release of acetone.<sup>14</sup> Reductive elimination releases **4a** and then regenerates the Pd(0) catalyst. The resulting **4a** is again engaged in oxidative addition to Pd(0). The reaction may involve the concerted metalation/deprotonation (CMD) process,<sup>15</sup> which could be a rate-determining step. Indeed, the acidity of the reactive C–H bond on a benzene ring greatly affects the efficiency of such reactions (*vide supra*). The CMD pathway forms a seven-membered palladacycle intermediate **E**, from which reductive elimination delivers the desired product **3a**.<sup>16,17</sup>

The sequential decarbonylative coupling/intramolecular C–H arylation proved to be broad in scope as evidenced by the various substituted triphenylenes **3** that could be prepared, as shown in Table 3. Although the reactions of **1e** and **1f** proceeded well to give the corresponding triphenylenes **3b** and **3c** (entries 2 and 3), the reaction of **1g**

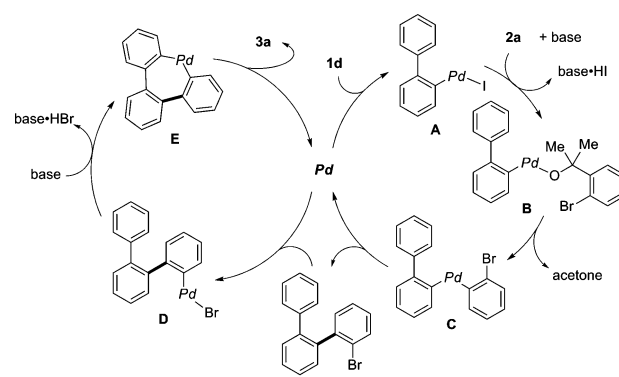
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(17) The reaction mechanism involving an aryne intermediate cannot be ruled out. In order to capture the possible aryne intermediate, the palladium-catalyzed reaction of **1d** with **2a** in the presence of an excess amount of a dienophile, furan, was investigated. However, the Diels–Alder reaction did not proceed at all and the desired triphenylene **3a** was obtained in 70% yield.

**Scheme 1.** A Plausible Mechanism of Formation of Triphenylene (**3a**)



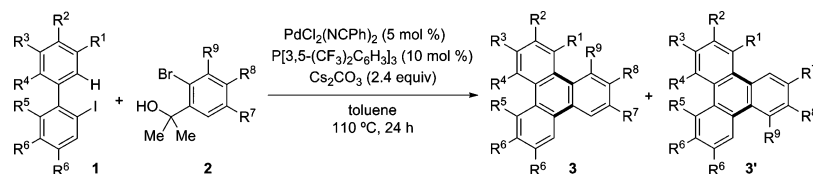
proceeded in decreased yield (entry 4). The reaction was found to be sensitive to a steric bulk at the reaction site of **1**. Thus, the sterically hindered **3e** was obtained in only 28% yield (entry 5). When the substrate **1i** having two reaction sites was employed, the less hindered C–H bond predominantly underwent reaction to yield **3b** in preference to **3d** (entry 6). Reactions of aryl iodides **1j–1n** bearing electron-donating and -withdrawing groups proceeded smoothly to give the desired products **3f–3j** (entries 7–11). Notably, reactions of electron-deficient aryl halides gave higher yields than those of electron-rich compounds (entries 7–11 vs entry 12). Rotation along the biphenyl axis is restricted in **1p** which provided **3l** in 23% yield (entry 13). Reaction of **1d** with substituted *o*-bromobenzyl alcohols **2d–2f** afforded **3k**, **3m**, and **3n** in good yields (entries 15–17). The Pd-catalyzed annulation with the naphthalene-containing substrate **2g** gave the benzochrycene derivative **3o**, albeit in low yield, demonstrating the feasibility of this reaction to these potentially useful PAHs (entry 18).<sup>18</sup>

The multisubstituted triphenylenes were successfully synthesized by reaction of **1** with **2d**. The reaction of **1j** provided a mixture of regioisomers **3p** and **3p'** in a 1:1 ratio (entry 19).<sup>19</sup> Although we also observed no regioselectivity in the reaction of electron-rich **1i** (entry 20), to our delight, the use of aryl iodide **1h** crowded at the reaction site improved the regioselectivity up to 9:1 (entry 21). Notably, the steric sensitivity of the reaction that inhibits the product formation was also observed in the reaction of **1h** with **2d**. Interestingly, in one case regioisomer **3s'** was formed in preference to **3s** from **1q** and **2d** (entry 22).

Formation of a mixture of two regioisomers can be rationalized by the following working hypothesis. After oxidative addition of **1**, an arylpalladium complex undergoes

(18) The present reaction was greatly influenced by the efficiency of the second C–C bond formation step, which was determined by the electronic and steric properties of **1** and **2**. When the second coupling was slow, the catalyst would be deactivated to leave a measurable amount of **4** (entries 4, 5, 13, and 18).

(19) While the reaction was performed at 90 °C, the target triphenylenes **3p** and **3p'** were obtained in 8% yield in the same ratio of 1:1 and the starting *o*-iodobiphenyl **1j** was recovered unchanged.

**Table 3.** Substrate Scope of Reactions of *o*-Iodobiphenyls **1** with *o*-Bromobenzyl Alcohols **2**<sup>a</sup>

entry	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	R <sup>6</sup>	<b>1</b>	R <sup>7</sup>	R <sup>8</sup>	R <sup>9</sup>	<b>2</b>	product	yield (%) <sup>b</sup>
1	H	H	H	H	H	H	<b>1d</b>	H	H	H	<b>2a</b>	<b>3a</b>	81
2	H	Me	H	H	H	H	<b>1e</b>	H	H	H	<b>2a</b>	<b>3b</b>	65
3	H	Ph	H	H	H	H	<b>1f</b>	H	H	H	<b>2a</b>	<b>3c</b>	47
4	H	H	H	Me	H	H	<b>1g</b>	H	H	H	<b>2a</b>	<b>3d</b>	38
5	Me	H	Me	H	H	H	<b>1h</b>	H	H	H	<b>2a</b>	<b>3e</b>	28
6	H	H	Me	H	H	H	<b>1i</b>	H	H	H	<b>2a</b>	<b>3b:3d = 4:1<sup>c</sup></b>	62 <sup>d</sup>
7	H	NO <sub>2</sub>	H	H	H	H	<b>1j</b>	H	H	H	<b>2a</b>	<b>3f</b>	92
8	H	CF <sub>3</sub>	H	H	H	H	<b>1k</b>	H	H	H	<b>2a</b>	<b>3g</b>	92
9	H	F	H	H	H	H	<b>1l</b>	H	H	H	<b>2a</b>	<b>3h</b>	81
10	H	Cl	H	H	H	H	<b>1m</b>	H	H	H	<b>2a</b>	<b>3i</b>	50
11	H	COOMe	H	H	H	H	<b>1n</b>	H	H	H	<b>2a</b>	<b>3j</b>	72
12	H	OMe	H	H	H	H	<b>1o</b>	H	H	H	<b>2a</b>	<b>3k</b>	50
13	H	H	H	-CH <sub>2</sub> -O-	H	H	<b>1p</b>	H	H	H	<b>2a</b>	<b>3l</b>	23
14	H	H	H	H	H	OMe	<b>1q</b>	H	H	H	<b>2a</b>	<b>3m</b>	61
15	H	H	H	H	H	H	<b>1d</b>	OMe	H	H	<b>2d</b>	<b>3k</b>	82
16	H	H	H	H	H	H	<b>1d</b>	OMe	OMe	H	<b>2e</b>	<b>3m</b>	63
17	H	H	H	H	H	H	<b>1d</b>	-O-CH <sub>2</sub> -O-	H	H	<b>2f</b>	<b>3n</b>	55
18	H	H	H	H	H	H	<b>1d</b>	H	-CH=CH-CH=CH-	H	<b>2g</b>	<b>3o</b>	31
19	H	NO <sub>2</sub>	H	H	H	H	<b>1j</b>	OMe	H	H	<b>2d</b>	<b>3p:3p' = 1:1<sup>c</sup></b>	82 <sup>d</sup>
20	H	OMe	H	H	H	H	<b>1o</b>	OMe	H	H	<b>2d</b>	<b>3q:3q' = 1:1<sup>c</sup></b>	48 <sup>d</sup>
21	Me	H	Me	H	H	H	<b>1h</b>	OMe	H	H	<b>2d</b>	<b>3r:3r' = 9:1<sup>c</sup></b>	28 <sup>d</sup>
22	H	H	H	H	H	OMe	<b>1q</b>	OMe	H	H	<b>2d</b>	<b>3s:3s' = 1:2<sup>c</sup></b>	54 <sup>d</sup>

<sup>a</sup> Conditions: **1** (0.5 mmol), **2** (0.6 mmol), PdCl<sub>2</sub>(NCPh)<sub>2</sub> (0.025 mmol), P[3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>3</sub> (0.05 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (1.2 mmol) in toluene (2 mL).  
<sup>b</sup> Isolated yields. <sup>c</sup> Determined by the <sup>1</sup>H NMR analyses. <sup>d</sup> Combined yields of two regioisomers.

the reaction with **2** to yield the expected triphenylene **3**. Meanwhile, an intramolecular 1,4-palladium shift<sup>20</sup> can compete with the reaction with **2**. The reaction of the other arylpalladium complex with **2** thus provides regioisomer **3'**. In the case of **1j** and **1l**, a 1:1 mixture of regioisomers was obtained because of rapid equilibration. Conversely, the regioselectivity of the reaction was dramatically increased with **1h**. In this case formation of **3r** predominated, and the origin of this selectivity can be explained by the steric factor. The disfavored intermediate has a steric repulsion between a methyl group and palladium, while the favored intermediate smoothly undergoes the reaction with **2d** to yield **3r** selectively. The preference of **3s'** to **3s** can be explained in the same way.

In conclusion, we have demonstrated that the annulation reaction of *o*-iodobiphenyls with *o*-bromobenzyl

alcohols in the presence of a palladium/phosphine catalyst provides a facile and straightforward entry to highly substituted triphenylenes. The reactions proceeded with high efficiency and compatibility of various functional groups. Syntheses of other synthetically useful PAHs by using annulation with *o*-bromobenzyl alcohols are currently under investigation in our laboratory.

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**Supporting Information Available.** Experimental procedures as well as characterization data for all the compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.

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