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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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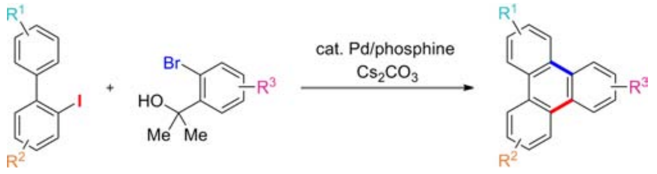
ABSTRACT



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 photophysical properties.[1] Among them, triphenylenes have garnered much interest and have been used to construct functional organic materials such as discotic liquid crystals[2,3] and organic light-emitting diodes.[4] 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.[5] To date, the standard synthetic method for the preparation of triphenylenes has been the

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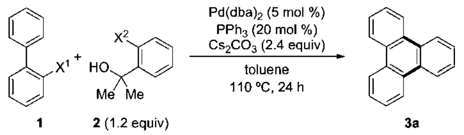
cyclization of *o*-terphenyls under severe acidic and/or oxidative conditions.[6] However, since many functional groups cannot tolerate such harsh reaction conditions, the scope of this triphenylene synthesis is limited. More recently, transition-metal catalyst-based approaches have attracted much attention as they offer synthetic routes that are highly efficient and compatible with various functional groups.[7,8] Nomura and Miura have reported two examples of substituted triphenylenes via the palladium-catalyzed annulation of *o*-dibromobenzenes with *o*-phenybenzyl alcohols.[9] Larock also reported the synthesis of substituted triphenylenes by the palladium-catalyzed annulation of *o*-iodobiphenyls with in situ generated arynes.[10] 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.[11]

We initially investigated the effect of halides in the annulation of *o*-halobiphenyls **1** with *o*-halobenzyl alcohols **2** (Table 1).[12] 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**[a]



entry	X^1	X^2	yield (%)[b]
1	Br (**1a**)	Br (**2a**)	15
2	Br (**1a**)	Cl (**2b**)	<1
3	Br (**1a**)	I (**2c**)	2
4	OTf (**1b**)	Br (**2a**)	0
5	Cl (**1c**)	Br (**2a**)	0
6	I (**1d**)	Br (**2a**)	26

[a] Conditions: **1** (0.25 mmol), **2** (0.3 mmol), Pd(dba)$_2$ (0.0125 mmol), PPh$_3$ (0.05 mmol), and Cs$_2$CO$_3$ (0.6 mmol) in toluene (1 mL). [b] Determined by the ^{1}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.[13] Trialkylphosphines such as PCy$_3$ (Cy = cyclohexyl) or P^{n}Bu$_3$, triphenylphosphite P(OPh)$_3$, 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)$_2$, PdCl$_2$, or PdCl$_2$(NCMe)$_2$, the reaction proceeded well (entries 5−7). Finally, PdCl$_2$(NCPh)$_2$ 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**[11a] were detected by the ^{1}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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(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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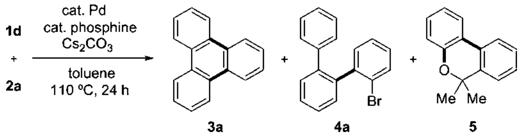
Table 2. Palladium-Catalyzed Annulation of *o*-Iodobiphenyl (**1d**) with *o*-Bromobenzyl Alcohol **2a**[a]



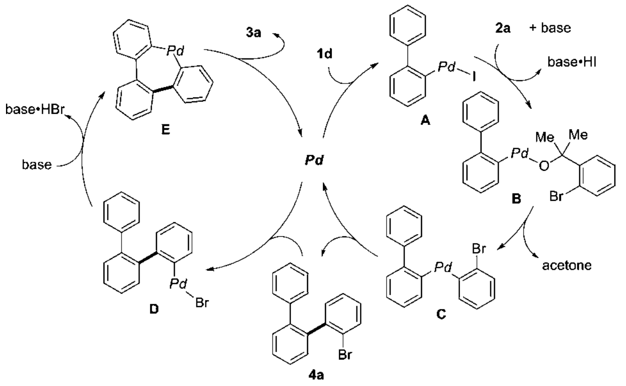
entry	Pd	phosphine	yield (%)[b] 3a	1d	4a	5
1	$Pd(dba)_2$	PPh_3	44	26	0	0
2		$P(4\text{-}MeOC_6H_4)_3$	35	42	0	0
3		$P[3,5\text{-}(CF_3)_2C_6H_3]_3$	47	0	0	19
4[c]			51	0	0	20
5	$Pd(OAc)_2$		45	0	10	17
6	$PdCl_2$		51	0	3	17
7	$PdCl_2(NCMe)_2$		51	0	0	23
8	$PdCl_2(NCPh)_2$		81	0	4	16

[a] Conditions: **1d** (0.25 mmol), **2a** (0.3 mmol), a Pd source (0.0125 mmol), phosphine ligand (0.05 mmol), and Cs_2CO_3 (0.6 mmol) in toluene (1 mL). [b] Determined by GC analysis of the crude mixture using hexadecane as an internal standard. [c] $P[3,5\text{-}(CF_3)_2C_6H_3]_3$ (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 β-carbon elimination delivers a diarylpalladium complex **C** with a release of acetone.[14] 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,[15] 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**.[16,17]

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**

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).[18]

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).[19] Although we also observed no regioselectivity in the reaction of electron-rich **1l** (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

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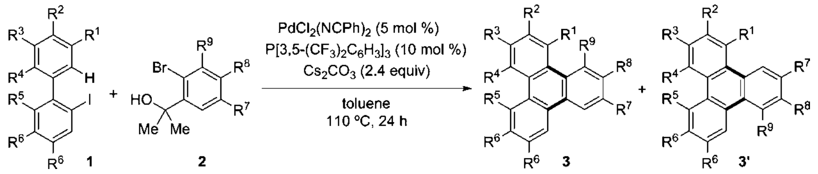
[16] For recent reviews of the intramolecular cyclization via palladium-catalyzed C–H arylation of aryl halides, see: (a) Chiusoli, G. P.; Catellani, M.; Costa, M.; Motti, E.; Della Ca', N.; Maestri, G. *Coordin. Chem. Rev.* **2010**, *254*, 456. (b) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174.

[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.

[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**[a]



entry	R^1	R^2	R^3	R^4	R^5	R^6	**1**	R^7	R^8	R^9	**2**	product	yield (%)[b]
1	H	H	H	H	H	H	**1d**	H	H	H	**2a**	**3a**	81
2	H	Me	H	H	H	H	**1e**	H	H	H	**2a**	**3b**	65
3	H	Ph	H	H	H	H	**1f**	H	H	H	**2a**	**3c**	47
4	H	H	H	Me	H	H	**1g**	H	H	H	**2a**	**3d**	38
5	Me	H	Me	H	H	H	**1h**	H	H	H	**2a**	**3e**	28
6	H	H	Me	H	H	H	**1i**	H	H	H	**2a**	**3b**:**3d** = 4:1[c]	62[d]
7	H	NO_2	H	H	H	H	**1j**	H	H	H	**2a**	**3f**	92
8	H	CF_3	H	H	H	H	**1k**	H	H	H	**2a**	**3g**	92
9	H	F	H	H	H	H	**1l**	H	H	H	**2a**	**3h**	81
10	H	Cl	H	H	H	H	**1m**	H	H	H	**2a**	**3i**	50
11	H	COOMe	H	H	H	H	**1n**	H	H	H	**2a**	**3j**	72
12	H	OMe	H	H	H	H	**1o**	H	H	H	**2a**	**3k**	50
13	H	H	H	$-CH_2-O-$		H	**1p**	H	H	H	**2a**	**3l**	23
14	H	H	H	H	H	OMe	**1q**	H	H	H	**2a**	**3m**	61
15	H	H	H	H	H	H	**1d**	OMe	H	H	**2d**	**3k**	82
16	H	H	H	H	H	H	**1d**	OMe	OMe	H	**2e**	**3m**	63
17	H	H	H	H	H	H	**1d**	$-O-CH_2-O-$		H	**2f**	**3n**	55
18	H	H	H	H	H	H	**1d**	H	$-CH=CH-CH=CH-$		**2g**	**3o**	31
19	H	NO_2	H	H	H	H	**1j**	OMe	H	H	**2d**	**3p**:**3p'** = 1:1[c]	82[d]
20	H	OMe	H	H	H	H	**1o**	OMe	H	H	**2d**	**3q**:**3q'** = 1:1[c]	48[d]
21	Me	H	Me	H	H	H	**1h**	OMe	H	H	**2d**	**3r**:**3r'** = 9:1[c]	28[d]
22	H	H	H	H	H	OMe	**1q**	OMe	H	H	**2d**	**3s**:**3s'** = 1:2[c]	54[d]

[a] Conditions: **1** (0.5 mmol), **2** (0.6 mmol), $PdCl_2(NCPh)_2$ (0.025 mmol), $P[3,5\text{-}(CF_3)_2C_6H_3]_3$ (0.05 mmol), and Cs_2CO_3 (1.2 mmol) in toluene (2 mL). [b] Isolated yields. [c] Determined by the ^1H NMR analyses. [d] Combined yields of two regioisomers.

the reaction with **2** to yield the expected triphenylene **3**. Meanwhile, an intramolecular 1,4-palladium shift[20] 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. Experimantal 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.

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The authors declare no competing financial interest.