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Imposing Curvature on a Polyarene by Intramolecular Palladium-Catalyzed Arylation Reactions: A Simple Synthesis of Dibenzo[*a*,*g*]corannulene

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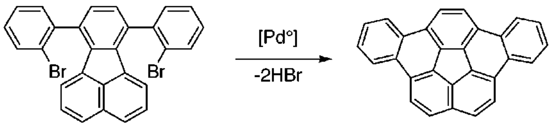
ABSTRACT



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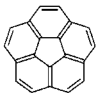
Palladium catalysis has been found to offer an effective solution-phase alternative to gas-phase flash vacuum pyrolysis as a method for converting the planar ring system of 7,10-di(2-bromophenyl)fluoranthene (4) to that of the $C_{28}H_{14}$ bowl-shaped fullerene fragment dibenzo[*a*,*g*]corannulene (5).

The synthesis and study of bowl-shaped polycyclic aromatic hydrocarbons (PAHs) whose networks of five- and six-membered rings can be mapped onto those of C_{60} and/or the higher fullerenes has attracted considerable attention in recent years.[1] Such geodesic polyarenes are characterized by both concave and convex π-surfaces as well as by a high degree of strain energy[2] resulting from the pyramidalization of interior trigonal carbon atoms. An ability to exhibit fullerene-like chemistry at their interior carbon atoms[1c,f,g] sets these novel hydrocarbons apart from their familiar planar relatives.

Some years ago, we introduced the use of flash vacuum pyrolysis (FVP) as a strategy for stitching together distantly separated carbon atoms in planar PAH derivatives to construct strained fullerene fragments.[3] Most subsequent synthetic work, both in our laboratory and elsewhere, has employed this powerful technique.[1] With appropriate pyrolysis precursors, the FVP method has been used to synthesize a broad range of geodesic polyarenes built around a central five-membered ring (e.g., corannulene **1**), a central alkene (e.g., the $C_{26}H_{12}$ bowl **2**), or a central six-membered ring (e.g., the chiral $C_{30}H_{12}$ bowl **3**).



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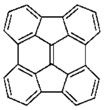

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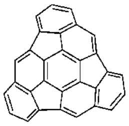

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Despite the obvious success of this method, the FVP strategy suffers from several drawbacks: (1) low to modest

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(1) Several reviews have already been published: (a) Rabideau, P. W.; Sygula, A. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI Press: Greenwich, 1995; Vol. 3, pp 1−36. (b) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235−242. (c) Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291−300. (d) Mehta, G.; Rao, H. S. P. *Adv. Strain Org. Chem.* **1997**, *6*, 139−187. (e) Mehta, G.; Rao, H. S. P. *Tetrahedron* **1998**, *54*, 13325−13370. (f) Scott, L. T.; Bronstein, H. E.; Preda, D. V.; Ansems, R. B. M.; Bratcher, M. S.; Hagen, S. *Atual. Fis.-Quim. Org.* **1999**, *11*, 138−150. (g) Scott, L. T.; Bronstein, H. E.; Preda, D. V.; Ansems, R. B. M.; Bratcher, M. S.; Hagen, S. *Pure Appl. Chem.* **1999**, *71*, 209−219.

(2) Kiyobayashi, T.; Nagano, Y.; Sakiyama, M.; Yamamoto, K.; Cheng, P.-C.; Scott, L. T. *J. Am. Chem. Soc.* **1995**, *117*, 3270−1.

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10.1021/ol005755p CCC: $19.00

Table 1. Reaction Conditions, Product Ratios, and Isolated Yields of Products from the Reaction in Scheme 2

entry	catalyst	base	solvent[a]	additive	conditions[b]	ratio (%)[c] 4	5	6	7	yield (%)[d]
1	$Pd(OAc)_2$	DBU	NMP	LiI	130 °C/48 h	100	0	0	0	**4** (95)
2	$Pd(OAc)_2$	DBU	NMP	LiI	175 °C/48 h	90	0	tr	10	
3	$Pd(OAc)_2$	DBU	NMP	Bu_4NBr	175 °C/48 h	90	0	tr	10	
4	$Pd(OAc)_2$	K_2CO_3	NMP	none	175 °C/48 h	75	0	tr	25	
5	$Pd[P(o\text{-tol})_3]_2Cl_2$	DBU	DMF	Bu_4NBr/PPh_3	130 °C/48 h	95	0	0	5	
6	$Pd[P(o\text{-tol})_3]_2Cl_2$	DBU	DMF	Bu_4NBr/PPh_3	150 °C/48 h	0	20	55	25	
7	$Pd[P(o\text{-tol})_3]_2Cl_2$	DBU	DMAc	none	175 °C/48 h	0	0	5	95	
8	$Pd_2(dba)_3/P(t\text{-Bu})_3$	DBU	DMF	none	150 °C/72 h	0	25	70	5	**5** (21) **6** (60)
9	$Pd_2(dba)_3/P(t\text{-Bu})_3$	Cs_2CO_3	DMF	none	150 °C/72 h	0	10	85	5	**5** (8)
10	$Pd(PPh_3)_2Br_2$	DBU	DMF	none	150 °C/72 h	0	55	25	20	**5** (51)
11	$Pd(PPh_3)_2Br_2$	DBU	DMF	PPh_3	150 °C/72 h	0	55	25	20	**5** (53)
12	palladacycle[e]	DBU	DMF	none	150 °C/72 h	0	60	20	20	**5** (57)
13	palladacycle	DBU	DMAc	none	165 °C/72 h	0	25	60	15	
14	palladacycle	DBU	NMP	none	175 °C/12 h	0	5	45	50	
15	$Pd_2(dba)_3$/BINAP	DBU	DMF	none	150 °C/72 h	100	0	0	0	**4** (93)
16	$Pd_2(dba)_3$/BINAP	DBU	DMAc	none	175 °C/72 h	90	0	0	10	
17	$Pd_2(dba)_3$	DBU	DMF	none	150 °C/72 h	0	0	0	100	**7** (93)
18	$Pd_2(dba)_3$	DBU	DMAc	none	175 °C/72 h	0	0	0	100	
19	$PdCl_2(MeCN)_2$	DBU	DMF	none	150 °C/72 h	0	0	0	100	**7** (96)

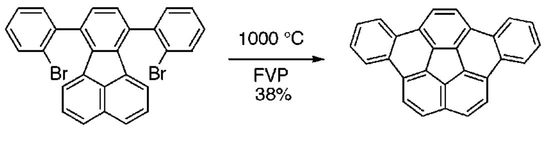
[a] Anhydrous solvents were purged with argon for 10 min. [b] A mixture of **4** (0.5 mmol), catalyst (10 mol %), base (40 mmol), and solvent (10 mL) was heated and stirred under argon. [c] Ratio determined by NMR integration and HPLC (reverse-phase RP-18, water−acetonitrile−CH_2Cl_2). tr = traces. [d] Isolated yield. [e] See ref 13.

yields, (2) essentially zero functional group tolerance, (3) a limitation to relatively small scale runs, and (4) the potential for thermal rearrangements of the molecular framework at the high temperatures normally employed (1000−1100 °C). In this regard, the new nonpyrolytic method reported by Seiders and Siegel et al. for preparing such compounds, using highly exothermic reductive couplings of benzylic bromides with Ti(0),[4] is especially noteworthy. Other workers in the field have been quick to adopt and extend this solution-phase alternative.[5] Herein we report our own, quite different, solution-phase alternative to the FVP method, one that is based on palladium-catalyzed intramolecular arylation reactions.[6]

Aryl−aryl coupling reactions involving palladium-catalyzed eliminations of HX (X = Br, I, OTf, etc.), both intra- and intermolecular, have enjoyed widespread popularity for the synthesis of carbocycles,[7] heterocycles,[8] and various natural products.[9] The mild reaction conditions, wide functional group tolerance, and infinite scaleability of this chemistry has made it very attractive for organic synthesis. To the best of our knowledge, however, catalytic palladium chemistry has never been successfully applied to the synthesis of a bowl-shaped polyarene; only one unsuccessful attempt has been reported.[10]

Shortly after finding that dibenzo[*a*,*g*]corannulene (**5**) could be prepared by FVP of 7,10-di(2-bromophenyl)-fluoranthene (**4**) (Scheme 1),[11,12] we began exploring palladium catalysis as a potential solution-phase alternative for the large scale preparation of **5** from the same precursor. Early results were encouraging, in that they gave detectable quantities of **5** [$Pd(OAc)_2$, K_2CO_3, Bu_4NBr, $(Ph)_3P$, DMF/H_2O, 100 °C, 90 h],[11c] thereby demonstrating the feasibility of this approach; however, we never succeeded in developing the reaction into a practical synthetic method at that time.

Scheme 1



4 **5**

Convinced that a preparatively useful palladium-catalyzed variant of the double cyclization in Scheme 1 should be possible, and impressed by the tremendous advances worldwide in organopalladium chemistry over the past several years, we recently resumed our activities in this area. Numerous palladium sources were screened, with both organic and inorganic bases, in several different dipolar aprotic solvents, with and without additives, at temperatures ranging from 130 to 175 °C (Table 1). The progress of the reactions was monitored by TLC and HPLC.

Gratifyingly, dibenzocorannulene (**5**) was indeed formed in several of the reactions. Unfortunately, reductive de-

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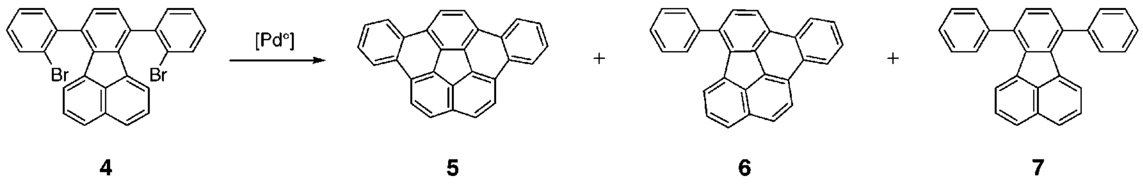
Scheme 2



bromination of the 2-bromophenyl groups, either just on one side, giving **6**, or on both sides, giving **7** (Scheme 2), often prevailed over the desired cyclizations.

It is clear from the results listed above that variations in the reaction conditions have a profound influence on the product distribution. The best yields of dibenzocorannulene (**5**) that we have achieved so far have come from the treatment of dibromide **4** with excess DBU and 10 mol % of either Pd(PPh$_3$)$_2$Br$_2$ or Herrmann's palladacycle[13] in dimethylformamide (DMF) at 150 °C (entries 10−12). The isolated yield of **5** under these conditions (50−60%) exceeds that obtained by the FVP method (35−40%) by a significant margin and gives hope that this chemistry could prove useful for the synthesis of other geodesic polyarenes.

It is interesting to note that the addition of triphenylphosphine had no influence on the product ratio in this catalytic reaction (compare entries 10 and 11) and that higher temperatures in either *N*-methylpyrrolidinone (NMP) or dimethylacetamide (DMAc) led to significantly more reductive debromination, with a corresponding decrease in the amount of dibenzocorannulene (**5**) formed (compare entries 12−14).

Notwithstanding our encouraging early results with Pd(OAc)$_2$ (vide supra), all subsequent experiments using this catalyst were completely unsuccessful. At temperatures lower than 150 °C in NMP, only starting material was recovered (entry 1). At high temperature, reductive debromination leading to diphenylfluoranthene **7** was the only reaction observed (entries 2−4). Neither LiI nor Bu$_4$NBr as additives promoted the desired cyclizations, and the use of K$_2$CO$_3$ as base simply accelerated the formation of **7** (entry 4).

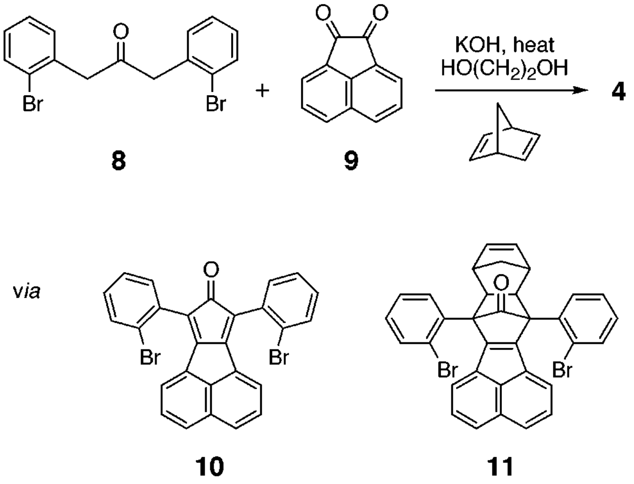
Only marginally greater success was achieved with Pd[P(*o*-tol)$_3$]$_2$Cl$_2$. With this catalyst, dibenzocorannulene (**5**) was formed in low yield at 150 °C in DMF (entry 6). At lower temperatures, however, only starting material was recovered (entry 5), whereas increasing the temperature to 175 °C led to reductive debromination and formation of **7** as the major product (entry 7).

With Pd[P(*t*-Bu)$_3$]$_2$, a catalyst known to be effective for palladium-catalyzed Heck and Suzuki couplings involving normally recalcitrant aryl chlorides,[14,15] 25% of the reaction took the desired course to produce **5** when DBU was used as the base (entry 8). The yield of **5** dropped significantly, however, when the inorganic base Cs$_2$CO$_3$ was used (entry 9). The major product obtained using Pd[P(*t*-Bu)$_3$]$_2$ was always the monoclosed hydrocarbon **6**.

The catalytic system Pd$_2$(dba)$_3$ and BINAP showed almost no reactivity; most of the starting material was recovered even after 72 h at 150−170 °C (entries 15 and 16). The use of phoshine-free Pd$_2$(dba)$_3$ and PdCl$_2$(MeCN)$_2$ led only to reductive debromination, yielding **7** nearly quantitatively (entries 17−19).

While the factors responsible for the success of the cyclizations listed in entries 10−12 remain uncertain, it is now clear that palladium-mediated dehydrobrominations can be used for intramolecular aryl−aryl couplings that generate strained geodesic polyarenes from relatively simple PAH derivatives. In the present case, dibromide **4** was prepared in just two steps from commercially available starting materials (Schemes 3 and 4).

Scheme 3



Taking advantage of our previously reported one-pot synthesis of 7,10-disubstituted fluoranthenes,[3] 1,3-di(2-bromophenyl)acetone (**8**) was heated with acenaphthene-

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(6) Aspects of this work have been reported in preliminary form: Scott, L. T.; Reisch, H. A. *Abstracts of Papers*, 219th National Meeting of the American Chemical Society, San Francisco, CA.; American Chemical Society: Washington, DC; March, 2000; ORGN-515.

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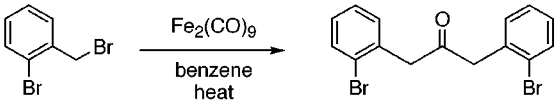
Scheme 4



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quinone (**9**) in the presence of a base and norbornadiene. A double Knoevenagel condensation reaction presumably generates cyclopentadienone **10**, which then undergoes a Diels–Alder reaction with the norbornadiene to give adduct **11**. Carbon monoxide and cyclopentadiene are lost spontaneously under the reaction conditions, giving **4** in 40% yield (Scheme 3). The entire assembly of the disubstituted fluoranthene takes place in a single reaction vessel without isolation of intermediates.

The 1,3-di(2-bromophenyl)acetone (**8**) required for this synthesis is easily prepared by carbonylation of 2-bromobenzyl bromide with diironnonacarbonyl[16] (71% yield) (Scheme 4).

By this three-step synthesis, dibenzo[*a*,*g*]corannulene (**5**) can now be prepared without pyrolysis in quantities sufficient to use as the starting point for syntheses of larger fullerene fragments.

Acknowledgment. We thank the National Science Foundation for financial support of this work.

Supporting Information Available: Characterization data for compounds **4**–**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) In the $Pd_2(dba)_3/P(t\text{-}Bu)_3$ system, $Pd[P(t\text{-}Bu)_3]_2$ is the only species observable by ^{31}P NMR spectroscopy, although recent studies indicate that $Pd[P(t\text{-}Bu)_3]_1$ is most likely the catalytically active species: Fu, G. C.; Littke, A. F.; Dai, C. *Book of Abstracts*, 219th National Meeting of the American Chemical Society, San Francisco, March 26–30, 2000; American Chemical Society: Washington, DC; 2000, ORGN-067.

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