ORGANIC
LETTERS

2004
Vol. 6, No. 20
3557−3560

Tris(benzocyclobutadieno)triphenylene and Its Lower Biphenylene Homologues by Palladium-Catalyzed Cyclizations of 2,3-Didehydrobiphenylene

Beatriz Iglesias, Agustín Cobas, Dolores Pérez,* and Enrique Guitián

Departamento de Química Orgánica, Universidade de Santiago de Compostela,
15782 Santiago de Compostela, Spain

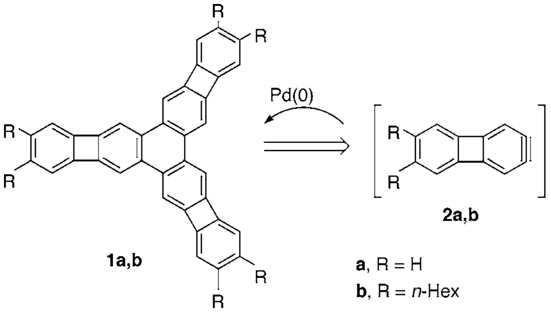
K. Peter C. Vollhardt*

Center for New Directions in Organic Synthesis, Department of Chemistry, University of California at Berkeley, and the Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720-1460

qodolopm@usc.es; kpcv@berkeley.edu

Received July 26, 2004

ABSTRACT



The Pd-catalyzed cycloaddition of didehydrobiphenylenes 2a,b, generated from the corresponding 3-(trimethylsilyl)-2-biphenylenyl triflates with fluoride, furnishes the C_3-symmetric trimers 1a,b in which the embedded triphenylene unit is distorted to increase the aromaticity of the central benzene ring. Cocylization of 2a,b with dimethyl acetylenedicarboxylate provides the phenanthrene- and naphthalenecarboxylic ester analogues, depending on the catalyst used.

The [*N*]phenylenes, polycyclic hydrocarbons comprised of alternating *N* benzene units fused to $N - 1$ cyclobutadiene rings, have been the subject of considerable attention because of their unique combination of aromatic and antiaromatic properties and their potential as molecular magnetic and/or conducting materials.[1] Among the variety of topologies acceded so far—linear,[2] angular,[3] zigzag,[4] and trigonal[5]—the C_3-symmetry of the latter is of particular interest, as it can led to orbital degeneracy, a characteristic of potentially ferromagnetic materials.[6]

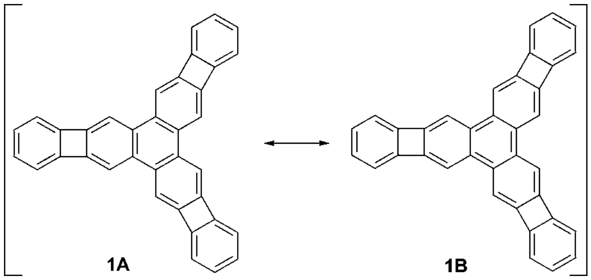
Especially intriguing in this connection is tris(benzocyclobutadieno)triphenylene (**1**), a molecule consisting of three biphenylene units fused to a central benzene ring. According to Clar,[7] triphenylene is "fully benzenoid", as it contains 6n π electrons and a unique Kekulé structure with all of the carbon atoms part of (outer) sextet rings. As such, the center benzene nucleus can be described as a triply benzofused cyclohexatriene. Distortion of triphenylene as in **1** should induce bond localization in its outer benzene rings and therefore reduce their aromaticity, possibly altering the Clar picture, in which resonance form A is dominant, toward a center sextet and more aromatic core, reflected in an

---

[1] Vollhardt, K. P. C.; Mohler, D. L. In *Advances in Strain in Organic Chemistry*; Halton, B., Ed.; JAI: London, 1996; Vol. 5, p 121.

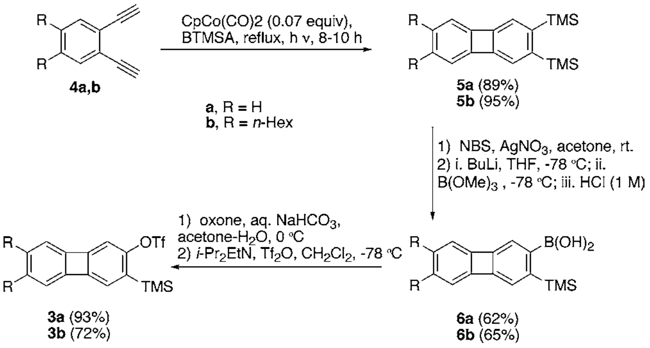
10.1021/ol048548o CCC: $27.50

increasing contribution of resonance form B. We describe the synthesis of **1a** and its substituted derivative **1b** by palladium-catalyzed cyclotrimerization of the corresponding 2,3-didehydrobiphenylenes **2a** and **2b**, respectively. These arynes participate also in Pd-catalyzed cocyclizations with dimethyl acetylenedicarboxylate (DMAD) to provide lower biphenylene homologues of **1**.



We have demonstrated recently the usefulness and broad applicability of Pd-catalyzed [2 + 2 + 2]cycloadditions of arynes for the preparation of polycyclic aromatic hydrocarbons (PAHs).[8,9] The exploitation of this methodology to the synthesis of **1a** required the availability of an adequate aryne precursor,[10] which, on the basis of our previous experience, should be 3-trimethylsilyl-2-biphenylenyl triflate (**3a**).

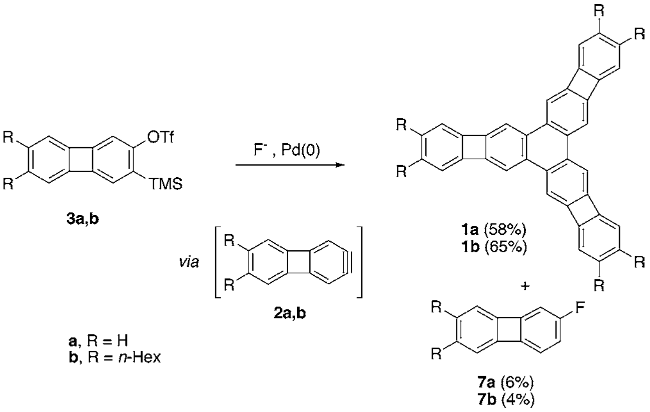
Scheme 1



The synthesis of **3a** was accomplished through the route shown in Scheme 1, featuring the construction of the biphenylene core through an efficient cobalt-mediated cycloaddition of **4a** to bis(trimethylsilyl)acetylene (BTMSA).[11] Selective replacement of one of the trimethylsilyl groups in **5a** by bromine (70% yield), followed by metal−halogen exchange, reaction with trimethoxyborane, and acidic work-up, yielded boronic acid **6a** in 89% yield. Oxidation with oxone afforded the corresponding biphenylenol which was treated with Tf_2O to give **3a** in 93% yield (a remarkable 52% overall yield from **4a**). A similar reaction sequence starting from 1,2-diethynyl-4,5-dihexylbenzene (**4b**)[12] led to triflate **3b** in a satisfactory 44% overall yield.[13]

Treatment of triflate **3a** with fluoride to generate aryne **2a**, under conditions established previously for the trimerization of polycyclic arynes [CsF (2 equiv), $Pd_2(dba)_3$ (0.1 equiv)],[8b−d] led to the instantaneous precipitation of a dark yellow solid that was insoluble in all common solvents and could not be purified or characterized. Gratifyingly, the use of $Pd(PPh_3)_4$ as catalyst and Bu_4NF as a soluble fluoride source allowed the isolation of **1a** in 58% yield as a bright yellow solid, which did not melt up to 400 °C (Scheme 2).

Scheme 2[a]



[a] Reaction conditions: (for **3a**) $Pd(PPh_3)_4$ (0.1 equiv), Bu_4NF (1 equiv, 0.1 M in 1:10 THF/CH_3CN, syringe addition over 1 h), CH_3CN, rt; (for **3b**) $Pd(PPh_3)_4$ (0.1 equiv), CsF (2 equiv), CH_3CN, rt, 10 h.

While highly insoluble, precluding the accumulation of ^{13}C NMR data, the structure of **1a** was readily ascertained

---

(2) (a) Blanco, L.; Helson, H. E.; Hirthammer, M.; Mestdagh, H.; Spyroudis, S.; Vollhardt, K. P. C. *Angew. Chem.*, Int. Ed. *Engl.* **1987**, *26*, 1246. (b) Hirthammer, M.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, *24*81.

(3) (a) Dosa, P. I.; Whitener, G. D.; Vollhardt, K. P. C.; Bond, A. D.; Teat, S. J. *Org. Lett.* **2002**, *4*, 2075. (b) Han, S.; Bond, A. D.; Disch, R. L.; Holmes, D.; Schulman, J. M.; Teat, S. J.; Vollhardt, K. P. C.; Whitener, G. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 3223. (c) Han, S.; Anderson, D. R.; Bond, A. D.; Chu, H. V.; Disch, R. L.; Holmes, D.; Schulman, J. M.; Teat, S. J.; Vollhardt, K. P. C.; Whitener, G. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 3227.

(4) Eickmeier, C.; Holmes, D.; Junga, H.; Matzger, A. J.; Scherhag, F.; Shim, M.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed.* **1999**, *38*, 800.

(5) (a) Diercks, R.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 3150. (b) Boese, R.; Matzger, A. J.; Mohler, D. L.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1478.

(6) (a) Breslow, R. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 199. (b) Tomaides, J.; Maslak, P.; Breslow, R. *J. Am. Chem. Soc.* **1988**, *110*, 3970.

(7) (a) Clar, E. *Polycyclic Hydrocarbons*; Academic Press Inc.: London, 1964; Vols. 1 and 2. (b) Clar, E. *The Aromatic Sextet*; Wiley: London, 1972. See also: (c) Moran, D.; Stahl, F.; Bettinger, H. F.; Schaefer, H. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2003**, *125*, 6746.

(8) Pd-catalyzed cyclotrimerization of arynes: (a) Peña, D.; Escudero, S.; Pérez, D.; Guitián, E.; Castedo, L. *Angew.* Chem., Int. Ed. **1998**, *110*, 2804. (b) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *Org. Lett.* **1999**, *1*, 1555. (c) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *Org. Lett.* **2000**, *2*, 1629. (d) Iglesias, B.; Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *Synlett* **2002**, 486.

(9) Pd-catalyzed cocycloaddition of arynes with alkynes: (a) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Am. Chem. Soc.* **1999**, *121*, 5827. (b) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Org. Chem.* **2000**, *60*, 6947.

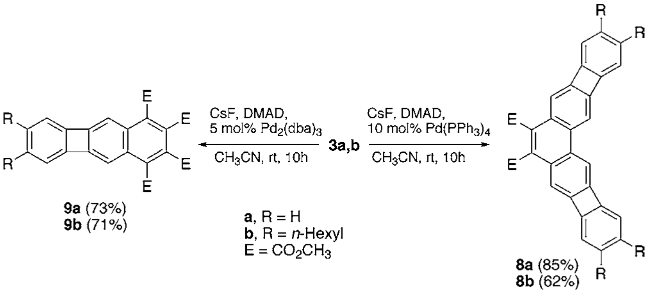
(10) 2,3-Dehydrobiphenylene has been generated previously from the corresponding diazonium carboxylate, but no cyclooligomers were detected: Losey, E. N.; LeGoff, E. *J. Org. Chem.* **1972**, *13*, 3812.

(11) Berris, B. C.; Hovakeemian, G. H.; Lai, Y.-H.; Mestdagh, H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1985**, *107*, 5670.

(12) Zhou, Q.; Carroll, P. J.; Swager, T. M. *J. Org. Chem.* **1994**, *59*, 1294.

(13) All new isolated compounds gave satisfactory analytical and/or spectral data.

Scheme 3



by its molecular cation and dication in the mass spectrum and the ^{1}H NMR spectrum in CS_2. In all the experiments, 2-fluorobiphenylene (**7a**), which results from nucleophilic attack of fluoride on aryne **2a**, was isolated in yields ranging from 6 to 20%. Cyclotrimerization of the 5,6-dihexyl derivative **3b** under similar conditions afforded **1b** in 65% yield. As expected, substitution with peripheral alkyl chains dramatically increased solubility, allowing **1b** to be chromatographed and fully characterized.

In the presence of dimethyl acetylenedicarboxylate (DMAD), arynes **2a**,**b** undergo [2 + 2 + 2]cocycloadditions to lower biphenylene homologues of **1**. Thus, treatment of **3a** (or **3b**) with CsF in the presence of catalytic amounts of $Pd(PPh_3)_4$ afforded the corresponding bis(benzocyclobutadieno)phenanthrenes **8a** (or **8b**) in 85 and 62% yield, respectively (Scheme 3).

The use of $Pd_2(dba)_3$ as the catalyst yielded as major products benzo[*b*]biphenylenes **9a** (73%) and **9b** (71%), the result of the cycloaddition of one aryne to two alkyne moieties. This chemoselectivity is in accord with that previously observed in cycloadditions of other arynes with DMAD.[9]

The ^{1}H NMR spectra of all new phenylene derivatives showed resonances at considerably higher field relative to those of their isolated aromatic segments. While the hydrogens in rings A of compounds **1**, **8**, and **9** occur in the range typical for the terminal rings of [*N*]phenylenes, shielding is more pronounced for hydrogens of the internal benzenes, pointing to a significant attenuation of the aromatic character in these rings. Thus, in **1**, H5 resonates at $\delta = 7.60$ (**1a**) and 7.40 (**1b**) ppm, with a $\Delta\delta \approx 1$ ppm relative to the typical chemical shift of the bay hydrogens in triphenylene (8.56 ppm).[14] A similar effect is observed in the spectra of **8** and **9** or, for better comparison, the known parent systems **10**[15] and **11**.[16] Figure 1 compiles experimental NMR and calculated NICS[17] and structural data[18] for **1**, **10**, and **11**[19] and compares them with those for triphenylene, phenanthrene, and naphthalene. Focusing on **1**, rings A and B resemble those in biphenylene structurally[20] and in their NICS values.[17a] The *Q* parameter[16b] for this segment is 0.914 (cf. biphenylene, 0.849), reflecting the antiaromaticity of cycle B. More instructive are the changes in C and D compared to triphenylene. Thus, as suggested above, C distorts even more than A to adopt a dimethylenecyclobutene frame, causing ring D to experience substantial bond equalization in the sense indicated by resonance form **1B**. At the same time, the NICS values signal and inversion of the relative aromaticity order, the core now being more diatropic than the attached periphery. The pronounced relative shielding of H5 can then be understood as reflecting the combined effects of the paratropism of ring B and the decreased diatropism of C (affecting this proton cumulatively, via direct attachment and across the bay region) outweighing the increased diatropism of the center. The same effects operate

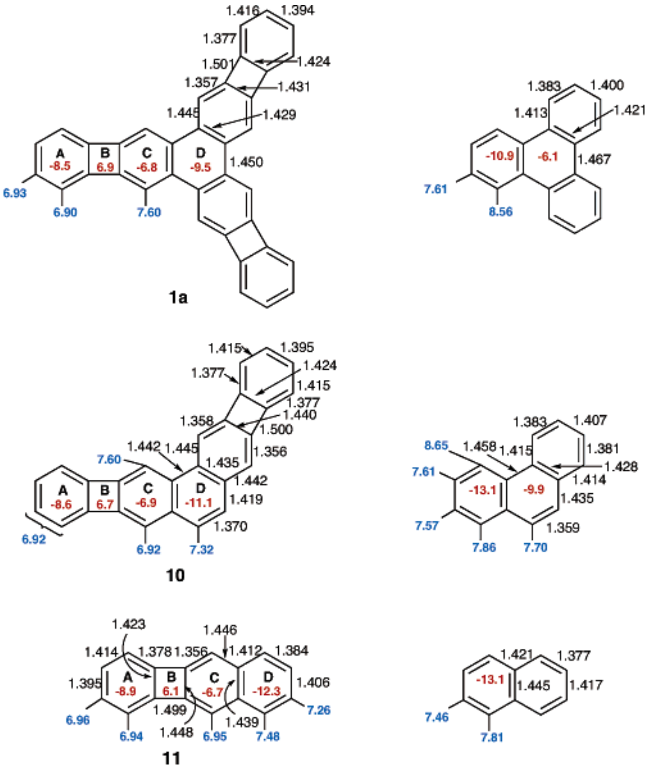


Figure 1. Experimental ^{1}H NMR chemical shifts (δ, ppm; blue), NICS (1.0) values (red), and calculated bond lengths (Å) for **1**, **10**, **11**, and reference benzenoids.

---

[14] Figeys, H. P.; Defay, N.; Martin, R. H.; McOmie, J. F. W.; Ayres, B. E.; Chadwick, J. B. *Tetrahedron* **1976**, *32*, 2571.

[15] Cracknell, M. E.; Kabli, R. A.; McOmie, J. F. W.; Perry, D. H. *J. Chem. Soc., Perkin Trans. 1* **1985**, 115.

[16] (a) Baker, W.; Barton, J. W.; McOmie, J. F. W.; Searle, R. J. G. *J. Chem. Soc.* **1962**, 2633. (b) For an analysis of this system, see: Andres, W.; Günther, H.; Günther, M.-E.; Hausmann, H.; Jikeli, G.; v. Puttkamer, H.; Schmickler, H.; Niu-Schwarz, J.; Schwarz, W. H. E. *Helv. Chim. Acta* **2001**, *84*, 1737.

[17] (a) Schulman, J. M.; Disch, R. L.; Jiao, H.; Schleyer, P. v. R. *J. Phys. Chem. A* **1998**, *102*, 8051. (b) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317. (c) Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2383.

[18] Geometries were optimized at B3LYP/6-31G* and used for NICS computations at HF/6-31G* (GIAO method). These methods have provided excellent agreement between calculated and experimental structural parameters of the [*N*]phenylenes: see, e.g., refs 3 and 4.

[19] The X-ray structure of **11** has been determined, but the utility of the data is limited by disorder problems: Ferrara, J. D.; Solooki, D.; Tessier-Youngs, C.; Youngs, W. *Acta Crystallogr.* **1989**, *C45*, 57.

[20] For a comparative analysis, see: Schleifenbaum, A.; Feeder, N.; Vollhardt, K. P. C. *Tetrahedron Lett.* **2001**, *42*, 7329.

in **10**, endowed with additional probes of the nonbay H5 ($\delta = 6.92$ ppm) and central ring H6 ($\delta = 7.32$ ppm). The former is shielded less than its same-ring bay region counterpart H13 ($\delta = 7.60$ ppm), as expected, the latter suffers from the dramatically reduced diatropicity of its neighbors more than it gains from the corresponding increase in ring D. Finally, **11** also conforms with this analysis, the new probe H6 ($\delta = 7.48$ ppm) experiencing slight shielding relative to its naphthalene counterpart because ring D is relatively less diatropic.

To conclude, the joint application of consecutive and chemoselective Co- and Pd-catalyzed alkyne cyclizations has opened the synthetic door potentially to a plethora of new π and σ activated, extended, conjugated frames that are of intrinsic theoretical interest and may have applications in materials science. As the *o*-bis(trimethylsilyl) motif exemplified by **5** is present in a number of phenylene derivatives,[1,2,4,5] we anticipate gaining access to a number of new topologies of these systems in the future.

Acknowledgment. This work was supported by the DGES (BQU2000-0464), PGIDT (01PXI20902PN), and NSF (CHE 0071887). B.I. acknowledges the Xunta de Galicia for a predoctoral fellowship. The Center for New Directions in Organic Synthesis is made possible by Bristol-Myers Squibb as a Sponsoring Member and Novartis as a Supporting Member.

Supporting Information Available: Experimental procedures, characterization of all new compounds, and XYZ files of calculated phenylenes. This material is available free of charge via the Internet at http://pubs.acs.org.

OL048548O