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Benzo[*a*]acecorannulene: Surprising Formation of a New Bowl-Shaped Aromatic Hydrocarbon from an Attempted Synthesis of 1,2-Diazadibenzo[*d,m*]corannulene

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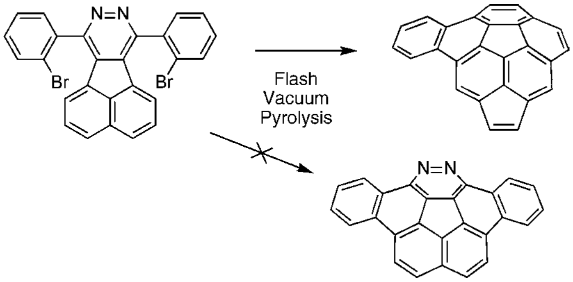
ABSTRACT



Flash vacuum pyrolysis of 7,10-bis(2-bromophenyl)acenaphtho[1,2-*d*]pyridazine ($C_{26}H_{14}Br_2N_2$) has resulted in a surprising transformation, including dinitrogen loss, to give benzo[*a*]acecorannulene, a novel $C_{26}H_{12}$ bowl-shaped fullerene fragment.

Since the introduction of flash vacuum pyrolysis[1] (FVP) as a new strategy for the synthesis of corannulene in 1991,[2] many geodesic polyarenes have been successfully synthesized using this versatile method.[3] Little success has been achieved, however, with the inclusion of heteroatoms in these fullerene fragments. The heterofullerene $C_{59}N$ has been studied extensively,[4] but smaller aza-buckybowls remain completely unknown, except to theoreticians.[5] The lone heterobuckybowl that has been successfully prepared contains sulfur atoms;[6] no nitrogen-containing aromatic bowl has been synthesized to date. Accordingly, we decided to examine

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(1) (a) Brown, R. F. C. *Pyrolytic Methods in Organic Chemistry: Application of Flow and Flash Vacuum Pyrolytic Techniques*; Academic Press: New York, 1980. (b) Brown, R. F. C. *Pure Appl. Chem.* **1990**, *62*, 1981. (c) McNab, H. *Aldrichimica Acta* **2004**, *37*, 19.

(2) (a) Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7082. (b) Scott, L. T.; Cheng, P.-C.; Hashemi, M. M.; Bratcher, M. S.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1997**, *119*, 10963.

(3) (a) Scott, L. T.; Bronstein, H. E.; Preda, D. V.; Ansems, R. B. M.; Bratcher, M. S.; Hagen, S. *Pure Appl. Chem.* **1999**, *71*, 209. (b) Scott, L. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 4994. (c) Tsefrikas, V. M.; Scott, L. T. *Chem. Rev.*, in press. (d) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235. (e) Mehta, G.; Rao, H. S. P. *Tetrahedron* **1998**, *54*, 13325.

(4) (a) Hirsch, A.; Nuber, B. *Acc. Chem. Res.* **1999**, *32*, 795. (b) Hummelen, J. C.; Bellavia-Lund, C.; Wudl, F. *Top. Curr. Chem.* **1999**, *199*, 93. (c) Nuber, B.; Hirsch, A. *Chem. Commun.* **1996**, 1421. (d) Hummelen, J. C.; Knight, B.; Pavlovich, J.; Gonzalez, R.; Wudl, F. *Science* **1995**, *269*, 1554.

(5) (a) Priyakumar, U. D.; Sastry, G. N. *J. Mol. Graphics Modell.* **2001**, *19*, 266. (b) Priyakumar, U. D.; Sastry, G. N. *J. Org. Chem.* **2001**, *66*, 6523. (c) Sastry, G. N.; Priyakumar, U. D. *J. Chem. Soc., Perkin Trans. 2* **2001**, 30.

(6) Imamura, K.; Takimiya, K.; Otsubo, T.; Aso, Y. *Chem. Commun.* **1999**, 1859.

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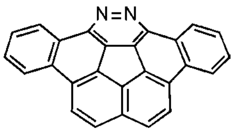
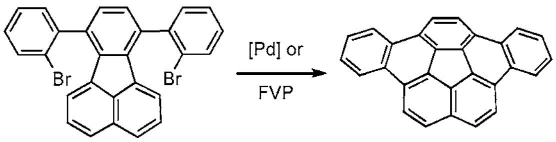
potential synthetic routes to the geodesic aza-polyarene 1,2-diazadibenzo[*d,m*]corannulene (**1**).



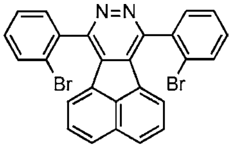
1

The choice of aza-bowl **1** as a synthetic target was strongly influenced by the success of two prior syntheses of the corresponding hydrocarbon, dibenzo[*a,g*]corannulene (eq 1).[7] In 2000, Scott et al. reported that both flash vacuum pyrolysis in the gas phase and palladium-catalyzed intramolecular arylation reactions in solution can be used to synthesize the bowl-shaped fullerene fragment.[7]



(1)

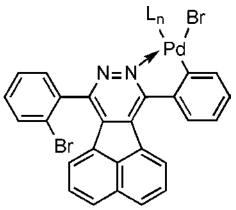
In light of this precedent, we have now synthesized the nitrogen-containing compound **2**, a potential precursor to **1**, which is analogous to the precursor used in the hydrocarbon route (eq 1), but with aza functionality built into the core. Details on the preparation of **2** are summarized at the conclusion of this letter.



2

For the synthesis of many corannulene derivatives, solution-phase reactions represent useful alternatives to flash vacuum pyrolysis.[7,8] Despite these advances, however, all attempts to close 7,10-bis(2-bromophenyl)acenaphtho[1,2-*d*]pyridazine (**2**) by the palladium-catalyzed intramolecular arylation method proved futile; unreacted starting material was recovered in all cases.

It is not known with certainty why the nitrogen-containing analogue (**2**) fails to react while its hydrocarbon counterpart can be successfully cyclized in 55% isolated yield.[7] One plausible explanation is that donation of the nitrogen lone pair into a vacant d orbital on the palladium locks the conformation as shown in **3**, thereby preventing the rotation required for cyclization across the bay region. Increasing the mole % of palladium catalyst leads to lower recovery of unreacted **2**, which suggests that **3** is stable under the reaction conditions and simply sequesters the catalyst.



3

In light of the failure of the palladium-catalyzed intramolecular arylation approach, flash vacuum pyrolysis of precursor **2** was investigated as a means to effect homolytic cleavage of the aryl−bromine bonds and bring about radical cyclizations to give the desired aza-bowl (**1**). In the gas-phase FVP synthesis of dibenzo[*a,g*]corannulene (eq 1), pyrolysis of 7,10-bis(2-bromophenyl)fluoranthene at 1050 °C gives a 38% isolated yield of the $C_{28}H_{14}$ bowl.[9] Considering the very harsh conditions, little hope was held for the retention of nitrogen during this process. Not surprisingly, exposure of precursor **2** to these conditions failed to give any detectable quantities of aza-bowl **1**. Interestingly, however, a single, unexpected major product was formed that could be isolated and characterized.

Analysis of the crude pyrolysate by mass spectrometry revealed a molecular ion at m/z 324. This mass corresponds to the molecular formula $C_{26}H_{12}$, which was confirmed by HRMS and differs from the molecular formula of the desired target compound (**1**, $C_{26}H_{12}N_2$) by two nitrogen atoms. Apparently, the harsh pyrolysis conditions not only induce the loss of two HBr molecules from the starting material but also cause dinitrogen expulsion to produce the hydrocarbon, $C_{26}H_{12}$. Loss of N_2 from pyridazines under pyrolysis conditions has previously been observed on many occasions.[10]

NMR spectroscopy provides all the additional information necessary to assign the structure of the hydrocarbon product as benzo[*a*]acecorannulene (**4**). The ^1H NMR spectrum (Figure 1) contains diagnostic signals for structural features that have previously been identified in the closely related bowl-shaped aromatic hydrocarbons acecorannulene (**5**)[11] and benzo[*a*]corannulene (**6**).[12]

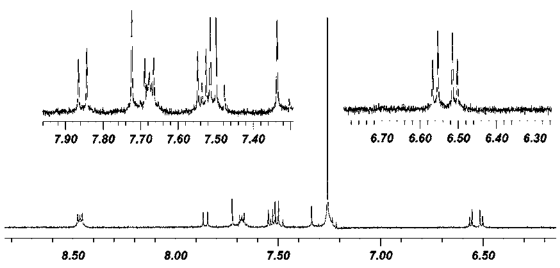


Figure 1. ^1H NMR spectrum of benzo[*a*]acecorannulene (**4**).

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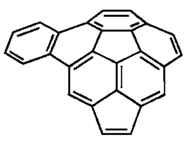
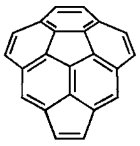
[7] Reisch, H. A.; Bratcher, M. S.; Scott, L. T. *Org. Lett.* **2000**, *2*, 1427.

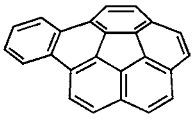
[8] (a) Seiders, T. J.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 2754. (b) Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **2000**, *122*, 6323.



4



5



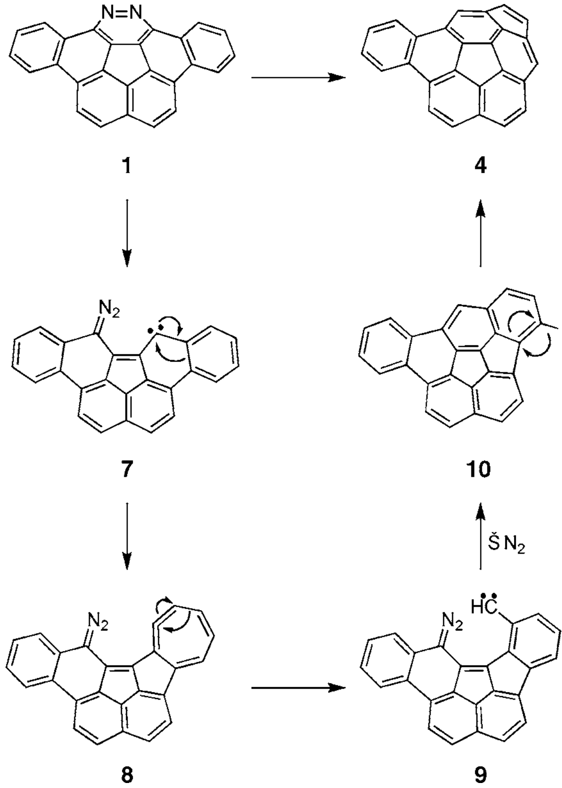
6

To begin with, the pair of narrow doublets appearing upfield of chloroform at δ 6.56 and 6.51 (J = 5.2 Hz) signifies the presence of an unsaturated, external five-membered ring; for comparison, the corresponding signal in the ^{1}H NMR spectrum of acecorannulene (**5**)[11] appears at δ 6.49 (s, 2H). The fact that two doublets are observed in the ^{1}H NMR spectrum of the isolated product, instead of a singlet, further indicates a lack of symmetry. Furthermore, the singlet at δ 7.53 appears in the same chemical shift range as that for the singlet from the hydrogens α to the five-membered ring on the core of acecorannulene (**5**, δ 7.38).[11] Finally, the pair of two-hydrogen multiplets at δ 8.47 and 7.68 in the ^{1}H NMR spectrum is similar in chemical shift and fine structure to the AA′BB′ pattern (δ 8.68 and 7.76) in the spectrum of benzo[*a*]corannulene (**6**),[12] suggesting that the new $C_{26}H_{12}$ ring system has a benzo group annulated to its core. On the basis of these spectral data, the only plausible chemical structure for the major product obtained from pyrolysis of **2** is benzo[*a*]acecorannulene (**4**).

Like acecorannulene (**5**), hydrocarbon **4** exhibits a high sensitivity to alumina and silica gel, which imposes significant losses of material with each chromatography. From the material balance and the ^{1}H NMR spectrum of the initial pyrolysate, we estimate the actual yield of **4** to fall in the range of 15−20%. Material purified to the level of that shown in Figure 1 was obtained in low yield by semi-preparative HPLC.

Although the mechanism for formation of this unexpected product is not immediately obvious, one possibility is outlined in Scheme 1. This proposal suggests that the desired aza-bowl (**1**) is, in fact, formed as the initial product but that the molecule is too unstable at high temperatures to survive.[10] Cleavage of one aryl−nitrogen bond would generate carbene **7**, which could shuffle its carbon atoms in a Jones rearrangement,[13] via **8**, to give the isomeric phenyl carbene **9**. A subsequent cyclization with loss of dinitrogen would lead to hydrocarbon **10**. From there, a well-precedented five/six-ring swap rearrangement[14] would separate the five-membered rings from each other and ultimately produce the stable product, benzo[*a*]acecorannulene (**4**). Variations on this mechanism that involve earlier loss of dinitrogen would also account for the observed results.[15]

Scheme 1



The 7,10-bis(2-bromophenyl)acenaphtho[1,2-*d*]pyridazine (**2**) used for these experiments was synthesized using Boger's 1,2,4,5-tetrazine→1,2-diazine strategy.[16] This involved the synthesis and inverse electron demand Diels−Alder (IEDDA) reaction of the acenaphthenone-derived enamine **17** and 3,6-bis(2-bromophenyl)-1,2,4,5-tetrazine (**16**) (Scheme 2).

The synthesis of 1,2,4,5-tetrazine **16** was achieved using an approach originally developed by Stollé.[17] Thus, acylation of acylhydrazine **10** with 2-bromobenzoyl chloride (**11**) afforded diacylhydrazine **12**. Reaction of **12** with PCl_5 gave a mixture of 1,3,4-oxadiazole **13** (31%) and bis(chloroimine) **14** (36%). The formation of two products is an interesting contrast to analogous syntheses of diaryl-1,2,4,5-tetrazines by Heuschmann, in which either the bis(chloroimine) or the 1,3,4-oxadiazole was obtained depending upon the steric requirements of the aryl groups.[18] This was expected to be of little consequence in view of Heuschmann's report that

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(9) (a) Bratcher, M. S. Ph.D. dissertation, Boston College, 1996. (b) Bratcher, M. S.; Scott, L. T. *Abstracts of Papers*, 207th National Meeting of the American Chemical Society; American Chemical Society: Washington, D. C.: San Diego, CA, March 1994; abstr ORGN 420.

(10) See, for example: (a) MacBride, J. A. H. *J. Chem. Soc., Chem. Commun.* **1972**, 1219. (b) Barton, J. W.; Rowe, D. J. *Tetrahedron Lett.* **1983**, *24*, 299. (c) Wilcox, C. F., Jr.; Lassila, K. R.; Kang, S. *J. Org. Chem.* **1988**, *53*, 4333.

(11) Sygula, A.; Abdourazak, A. H.; Rabideau, P. W. *J. Am. Chem. Soc.* **1996**, *118*, 339.

(12) (a) Mehta, G.; Srirama Sarma, P. V. V. *Chem. Commun.* **2000**, 19. (b) Peng, L.; Scott, L. T. *J. Am. Chem. Soc.* **2005**, *127*, 16518.

(13) Gaspar, P. P.; Hsut, J.-P.; Chari, S.; Jones, M., Jr. *Tetrahedron* **1985**, *41*, 1479.

(14) (a) Scott, L. T.; Roelofs, N. H. *J. Am. Chem. Soc.* **1987**, *109*, 5461. (b) Scott, L. T.; Roelofs, N. H. *Tetrahedron Lett.* **1988**, *29*, 6857. (c) Scott, L. T.; Hashemi, M. M.; Schultz, T. H.; Wallace, M. B. *J. Am. Chem. Soc.* **1991**, *113*, 9692. (d) Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291. (e) Necula, A.; Scott, L. T. *J. Anal. Appl. Pyrolysis* **2000**, *54*, 65.

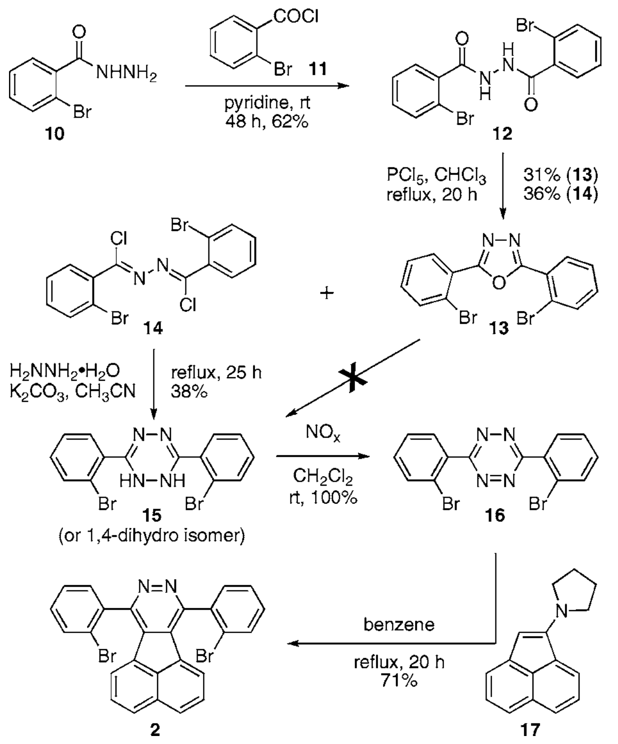
(15) One such alternative has been suggested by a referee, and a slightly modified version of this proposal is included in the Supporting Information. We emphasize that both proposed mechanisms are speculative and that at least one of them is incorrect.

(16) (a) Boger, D. L. *J. Heterocycl. Chem.* **1996**, *33*, 1519. (b) Boger, D. L. *Bull. Soc. Chim. Belg.* **1990**, *99*, 599. (c) Boger, D. L.; Weinreb, S. M. *Hetero Diels-Alder Methodology in Organic Synthesis*; Academic Press: New York, 1989. (d) Boger, D. L. *Chem. Rev.* **1986**, *86*, 781. (e) Boger, D. L. *Tetrahedron* **1983**, *39*, 2869.

(17) Stollé, R. *J. Prakt. Chem.* **1906**, *73*, 277.

(18) Hartmann, K.-P.; Heuschmann, M. *Tetrahedron* **2000**, *56*, 4213.

Scheme 2



both species react smoothly with hydrazine hydrate to afford the corresponding dihydro-1,2,4,5-tetrazines. However, 1,3,4-oxadiazole **13** was found to be unreactive and bis(chloroimine) **14** gave only a modest yield of the desired dihydrotetrazine **15**[19] (38%). Oxidation of **15** with nitrous gases cleanly afforded 3,6-bis(2-bromophenyl)-1,2,4,5-tetrazine (**16**).[20] Enamine **17** was generated upon reaction of acenaphthenone[21] with 5 equiv of pyrrolidine and reacted immediately without purification with tetrazine **16**. This delivered 7,10-bis(2-bromophenyl)acenaphtho[1,2-*d*]pyridazine (**2**) in 71% yield. Gram quantities of **2** could be prepared comfortably using this approach.

Herein, we have reported the formation of a new geodesic polyarene, benzo[*a*]acecorannulene (**4**), as the major isolable product from flash vacuum pyrolysis of 7,10-bis(2-bromophenyl)acenaphtho[1,2-*d*]pyridazine (**2**) at 1050 °C. The desired aromatic aza-bowl, 1,2-diazadibenzo[*d*,*m*]corannulene (**1**), could not be found among the products but may have been an intermediate on the pathway leading to **4**. Attempts to effect the conversion of **2** to **4** by palladium-catalyzed intramolecular arylation reactions in solution gave only recovered starting material.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council (NSERC) of Canada and the U.S. National Science Foundation for financial support of this work. We are grateful to one of the reviewers for his/her proposed mechanism for the formation of **4**, a slightly modified version of which appears in the Supporting Information.

Supporting Information Available: Experimental procedures and characterization data for new compounds. ^{1}H and ^{13}C NMR spectra for compounds, **2**, **4**, and **12**−**16**. UV−vis spectrum for compound **2**. An alternative proposed mechanism for the formation of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[19] Only one dihydro-1,2,4,5-tetrazine is formed, but we could not determine whether this was the 1,2- or the 1,4-dihydro isomer. Heuschmann (ref 17) reported the formation of 1,2-dihydro-1,2,4,5-tetrazines in similar systems.

[20] Brooker, P. J.; Parsons, J. H.; Reid, J.; West, P. J. *Pestic. Sci.* **1987**, *18*, 179.

[21] Synthesized from 2-(naphthalen-1-yl)ethanoic acid by reaction with PPA or by conversion to the acid chloride followed by intramolecular Friedel−Crafts acylation.