From phenylenes to acenes: flash vacuum pyrolytic isomerization of angular [3]phenylene to benzo[*ghi*]fluoranthene

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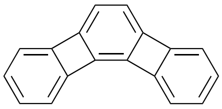
The flash vacuum pyrolysis of angular [3]phenylene and bis(2-ethynylphenyl)ethyne produces benzo[*ghi*]fluoranthene and chrysene, respectively.

Recently there has been much attention focused on the thermal interconversion of aromatic hydrocarbons because of its relevance to the formation of fullerenes[1] and environmental pollutants.[2] In connection with this, the fate of **1**[3] was of great interest because of its inherent strain and thus, its potential to equilibrate with its linear conterpart,[4] undergo retrocyclization to **2**,[5] or cascade into known $C_{18}H_{10}$ manifolds.[1,2]



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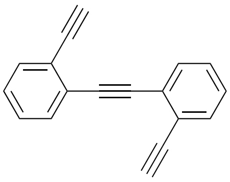
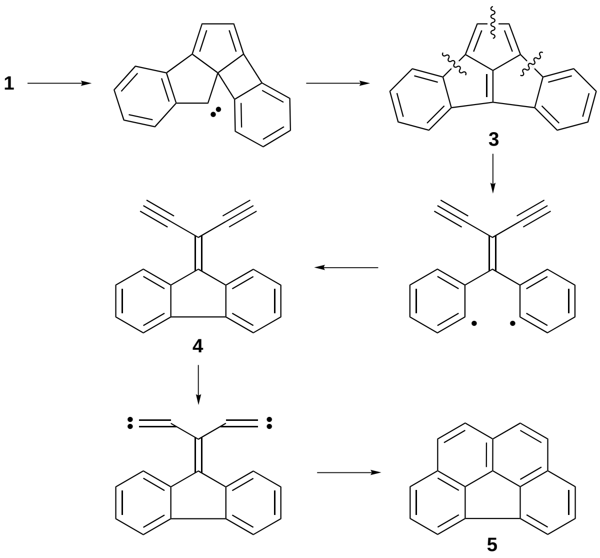


2

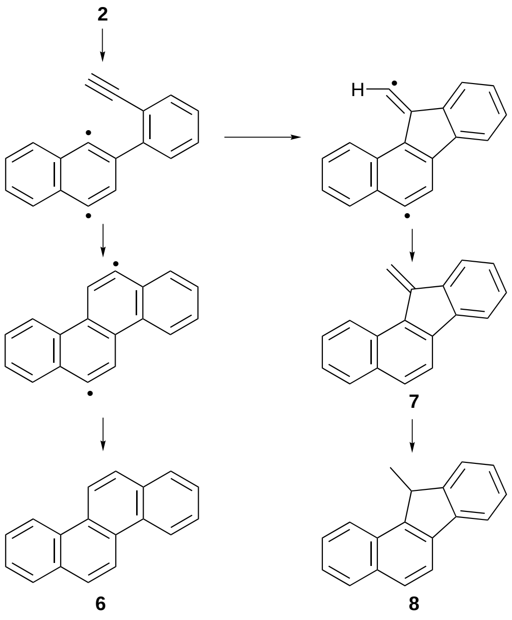
Initial experiments, in which **1** was sublimed through a quartz tube at 780 °C, resulted in essentially complete recovery of starting material. This result is not surprising, considering that **1** was first synthesized by pyrolytic methods at 800 °C.[6] Remarkably, however, at 1000 °C, the major isolable product was the unanticipated isomer benzo[*ghi*]fluoranthene **5** (10%),[7] in addition to minor quantities of chrysene ($C_{18}H_{12}$) **6** (2.5%) and fluoranthene ($C_{16}H_{10}$) (1%). A proposed mechanism for the transformation of **1** to **5** is outlined in Scheme 1. The first steps involve isomerization to dibenzoacepentalene **3**,[8] a formal Stone–Wales rearrangement.[1a] Stepwise or concerted cleavage of the five membered rings would afford diethynyldibenzofulvene **4** after phenyl radical recombination. The last two steps have their closest analogy in the synthesis of corannulene by flash vacuum pyrolysis (FVP) of an etheno-bridged, trimethylsilyl-protected derivative of **4**.[9]† The origin of chrysene may be **2** (*vide infra*). Significantly, **5** is not the product that might be expected on the basis of the results of the pyrolysis of biphenylene,[10] namely cyclopent[*hi*]acephenanthrylene (which has been shown to be inert to rearrangement to **5** under our conditions),[1d] presumably a consequence of the regioselectivity of the initial 1,2-shifts enforced by the proximity of the two four-membered rings.

As a control experiment, the FVP of **2** was executed. At 780 °C, all of the starting material had been consumed and chrysene **6** constituted the major isolated product (1.9% yield), none of **5** being present. A possible pathway from **2** to **6** is patterned after that proposed by Bergman in the solution thermolysis of the corresponding parent dienetriyne to form naphthalene (Scheme 2).[11] In the latter, the added hydrogen in the product is supplied by the solvent. The absence of an obvious hydrogen source in the FVP of **2** explains the low yield of **6**. Deuterium labelling of the terminal triple bonds‡ supported the proposed mechanism by furnishing only $[5,11\text{-}^{2}H_{2}]$chrysene. Note that neither **1** nor **3** are formed even at 1000 °C.

To further corroborate the fate of **2**, it was heated in benzene solution (205 °C) in the presence of cyclohexa-1,4-diene. Surprisingly, the major product was not **6** (2.5%), but rather 11-methyl-11*H*-benzo[*a*]fluorene **8** (19%).[12]§ We propose that the initially formed 1,4-didehydronaphthalene from **2** bifurcates to not only undergo 6-*endo*-digonal but also 5-*exo*-digonal



Scheme 1



Scheme 2

closure to form the five membered ring (Scheme 2). The resultant diradical would then be capped with hydrogen from cyclohexa-1,4-diene to provide the reactive fulvene **7** which undergoes fast transfer hydrogenation under the reaction conditions to yield **8**.[13] Further evidence for the intermediacy of **7** is found in the thermolysis of **2** in MeOH at 217 °C, in which the methyl group of the solvent is the hydrogen source. In this case 11-(2-hydroxyethyl)-1*H*-benzo[*a*]fluorene¶ is formed (26%) along with **6** (4.3%). This product is suggested to arise by trapping of **7** with $^{\bullet}CH_2OH$, followed by H abstraction from MeOH. The absence of products arising from 5-*exo* closure in the gas phase pyrolysis suggests that equilibration of the two diradicals to give the more stable didehydrochrysene is rapid under the conditions employed and/or that decomposition of the dibenzofulvene occurs in the absence of a good hydrogen donor.

Finally, we note that the observed conversion of phenylene **1** to the cyclopenta fused polycyclic benzenoid **5** constitutes the first of a series of potential conversions of larger phenylenes to semifullerenes.

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Footnotes

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† This report describes **5** as a side product, resulting from loss of C_2. Consistent with this finding is our observation of fluoranthene in the pyrolysis of **1**.

‡ Synthesized from bis[2-(trimethylsilylethynyl)phenyl]ethyne using MeOD and K_2CO_3.

§ GC–MS indicates that most of the diradicals formed add to cyclohexadiene or benzene rather than being trapped as **4** or **5**, thus accounting for the low combined yield of these products (21.5%).

¶ 11-(2-Hydroxyethyl)-1*H*-benzo[*a*]fluorene: *m/z* (EI-MS) 260 (M^+, 71%), 242 (49), 241 (30), 229 (16), 228 (19), 226 (15), 215 (100); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.40 (dq, *J* 13.4, 6.7 Hz, 1 H), 2.69 (dtd, *J* 13.9, 7.1, 3.6 Hz, 1 H), 3.38 (m, 2 H), 4.55 (dd, *J* 7.0, 3.6 Hz, 2 H), 7.32 (t, *J* 7.3 Hz, 1 H), 7.40 (t, *J* 7.4 Hz, 1 H), 7.45 (t, *J* 7.5 Hz, 1 H), 7.55 (t, *J* 7.4 Hz, 1 H), 7.62 (d, *J* 7.4 Hz, 1 H), 7.80 (d, *J* 7.5 Hz, 1 H), 7.88 (m, 2 H), 7.92 (d, *J* 8.2 Hz, 1 H), 8.17 (d, *J* 7.3 Hz, 1 H); ν_{max}(neat)/cm^{-1} 3353, 3053, 2927, 1466, 1022, 909, 821, 760.

References

1 (*a*) L. T. Scott, *Pure Appl. Chem.*, 1996, **68**, 291; (*b*) P. W. Rabideau and A. Sygula, *Acc. Chem. Res.*, 1996, **29**, 235; (*c*) R. F. C. Brown and F. W. Eastwood, *Pure Appl. Chem.*, 1996, **68**, 261; (*d*) L. W. Jenneskens, M. Sarobe and J. W. Zwikker, *Pure Appl. Chem.*, 1996, **68**, 219.

2 U. E. Wiersum, *Janssen Chim. Acta*, 1992, **10**, 3.

3 R. Diercks and K. P. C. Vollhardt, *Angew. Chem.*, 1986, **98**, 268; *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 266.

4 B. C. Berris, G. H. Hovakeemian, Y.-H. Lai, H. Mestdagh and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, 1985, **107**, 5670.

5 R. Diercks and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, 1986, **108**, 3150

6 J. W. Barton and R. B. Walker, *Tetrahedron Lett.*, 1978, 1005.

7 W. Karcher, R. J. Fordham, J. J. Dubois, P. G. J. M. Glaude and J. A. M. Ligthart, *Spectral Atlas of Polycyclic Aromatic Compounds*, Reidel, Dordrecht, 1985.

8 The synthesis of acepentalene and its tribenzo derivative have recently been reported: R. Haag, D. Schröder, T. Zywietz, H. Jiao, H. Schwarz, P. von R. Schleyer and A. de Meijere, *Angew. Chem.*, 1996, **108**, 1413; *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1317; R. Haag, B. Ohlhorst, M. Noltemeyer, R. Fleischer, D. Stalke, A. Schuster, D. Kuck and A. de Meijere, *J. Am. Chem. Soc.*, 1995, **117**, 10474.

9 G. Zimmermann, U. Nuechter, S. Hagen and M. Nuechter, *Tetrahedron Lett.*, 1994, **35**, 4747; R. F. C. Brown, N. Choi, K. J. Coulston, F. W. Eastwood, U. E. Wiersum and L. J. Jenneskens, *Tetrahedron Lett.*, 1994, **35**, 4405.

10 U. E. Wiersum and L. W. Jenneskens, *Tetrahedron Lett.*, 1993, **34**, 6615.

11 K. N. Bharucha, R. M. Marsh, R. E. Minto and R. G. Bergman, *J. Am. Chem. Soc.*, 1992, **114**, 3120.

12 G. M. Badger, *J. Chem. Soc.*, 1941, 535.

13 The rapid hydrogenation of dibenzofulvene by a radical mechanism has been observed: T. E. Nalesnik, J. H. Freudenberger and M. Orchin, *J. Organomet. Chem.*, 1981, **221**, 193.

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