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Phenyl Migrations in Dehydroaromatic Compounds. A New Mechanistic Link between Alternant and Nonalternant Hydrocarbons at High Temperatures

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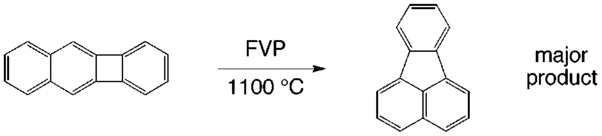
ABSTRACT

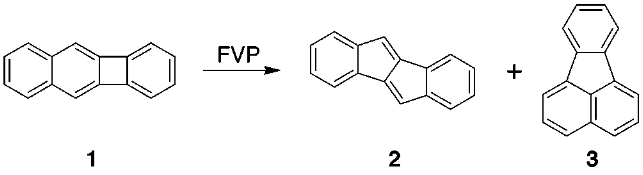


Flash vacuum pyrolysis of benzo[*b*]biphenylene, an alternant polycyclic aromatic hydrocarbon (PAH), gives fluoranthene, a nonalternant PAH, as the major product at 1100 °C in the gas phase. The most reasonable mechanism to explain this isomerization involves equilibrating diradicals of 2-phenylnaphthalene that rearrange by the net migration of a phenyl group to give equilibrating diradicals of 1-phenylnaphthalene, one isomer of which then cyclizes to fluoranthene.

In the course of developing a new and general method for the synthesis of indeno-fused polycyclic aromatic hydrocarbons (PAHs),[1] we encountered unexpected byproducts from the gas-phase pyrolysis of 2-bromobenzoyl PAHs that appeared to have arisen from phenyl group migrations around the perimeter of a polycyclic ring system. Mechanistically, the migration process could best be explained by a series of elementary steps consisting of reversible 1,5- and 1,6-hydrogen atom transfers (labeled as ∼H in the schemes that follow) and reversible intramolecular radical couplings to form transient biphenylene-type compounds, the whole sequence ending only when one of the intermediate aryl diradicals could finally close to form a relatively stable five- or six-membered ring. We now report more direct evidence for this type of "phenyl walk".

In an effort to uncover the simplest possible (nondegenerate) thermal migration of a phenyl group around the perimeter of a PAH diradical, we chose to examine the flash vacuum pyrolysis (FVP) of benzo[*b*]biphenylene (**1**).[2] At temperatures above 900 °C in the gas phase, two principal products are formed: indeno[2,1-*a*]indene (**2**) and fluoranthene (**3**) (Scheme 1).[3,4] The ratio of products **2** to **3** is 7:3 at 900 °C and 3:7 at 1100 °C.[5,6] Thus, isomerization to **2** is clearly favored at lower temperatures, but the pathway leading to **3** becomes dominant at higher temperatures.

Scheme 1



Temperature (°C)	Product Ratio (**2** : **3**)
900	7 : 3
1100	3 : 7

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(1) (a) Preda, D. V.; Scott, L. T. *Polycyclic Aromat. Compd.*, in press. (b) Scott, L. T.; Preda, D. V. *Abstracts of Papers*, 218th National Meeting of the American Chemical Society, New Orleans, LA, Aug, 1999; American Chemical Society: Washington, D C, 1999; ORGN-500. (c) Preda, D. V.; Scott, L. T. *Seventeenth International Symposium on Polycyclic Aromatic Compounds*, Bordeaux, France, Oct, 1999, abstract 138.

(2) (a) Jensen, F. R.; Coleman, W. E. *Tetrahedron Lett.* **1959**, No. 20, 7−11. (b) Baker, W.; Barton, J. W.; McOmie, J. F. W.; Searle, R. J. G. *J. Chem. Soc.* **1962**, 2633−6.

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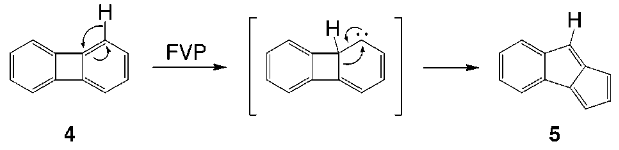
The rearrangement of **1** to **2** was not unexpected, as it closely resembles the known isomerization of biphenylene (**4**) to benzo[*a*]pentalene (**5**).[7] That skeletal reorganization can be viewed as a simple example of the well-known benzene ring contraction rearrangement,[6] driven by relief of strain in the four-membered ring (Scheme 2).

Scheme 2



The best evidence to date indicates that the benzene ring contraction rearrangement is not a concerted dyotropic process but proceeds in a stepwise manner through a carbene intermediate.[8] In the case of benzo[*b*]biphenylene (**1**), the ring contraction occurs exclusively in the naphthalene portion of the molecule, as expected on energetic grounds, to give indeno[2,1-*a*]indene (**2**) rather than naphtho[2,3-*a*]pentalene.

The formation of fluoranthene (**3**) from benzo[*b*]biphenylene (**1**) at high temperatures is difficult to explain without invoking a phenyl migration from the *β*-position of the naphthalene ring system to the α-position. This process is most likely initiated in the present case by homolytic cleavage of a strained C−C bond in **1** at high temperatures to generate a reactive diradical of 2-phenylnaphthalene (**6**).[9] From there, we propose a mechanistic pathway involving two successive 1,5-hydrogen atom transfers (discussed further below) to give an isomeric diradical (**8**) that is capable of cyclizing to benzo[*a*]biphenylene (**9**) (Scheme 3). Further isomerization to fluoranthene (**3**) could then proceed by a repeat of the same sequence of steps, viz., homolytic cleavage of a strained C−C bond in **9**, two successive intramolecular hydrogen atom transfers, and a final ring closure. A 1,6-hydrogen atom transfer is proposed to produce **11** from **10**, whereas the isomerizations of **6** to **7**, **7** to **8**, and **11** to **12** all involve 1,5-hydrogen atom transfers.

There is good experimental precedent for the isomerization of 1,2-aryl diradicals (*ortho*-benzynes) to 1,5-aryl diradicals by intramolecular hydrogen atom transfers of the sort proposed in Scheme 3,[6c,10,11] and 1,3-aryl diradicals (*meta*-benzynes) should behave similarly. Moreover, computational studies have shown that reversible intramolecular transfers of hydrogen atoms via five- and six-membered ring transition states are expected to be facile at high temperatures in aryl radicals.[12]

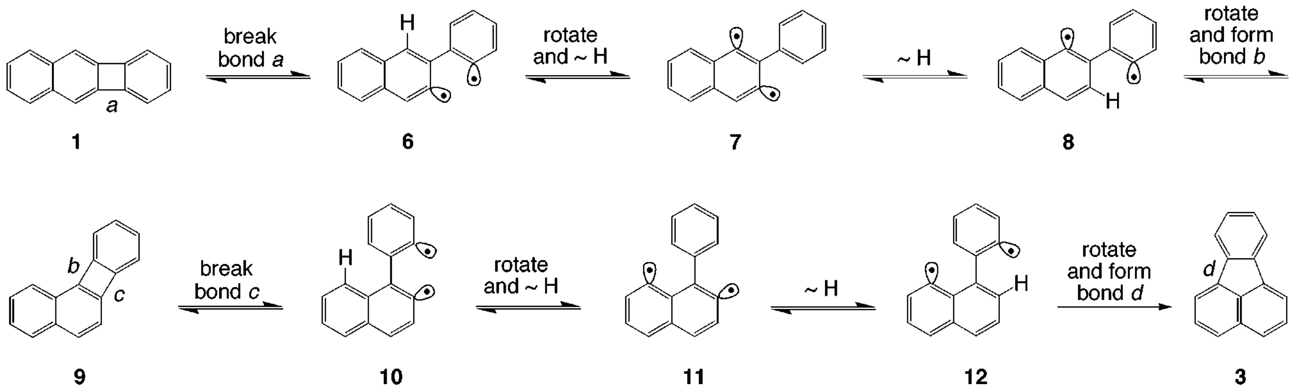
*The isomerization of 2-phenylnaphthalene-1,3-diyl (7) to 1-phenylnaphthalene-2,8-diyl (***11***) constitutes the net migration of a phenyl group in a dehydroaromatic compound that we set out to expose.*

To be absolutely complete, of course, this mechanistic picture should include a minor variant of Scheme 3 in which the benzene ring, rather than the naphthalene ring, serves as the temporary diradical moiety to progress from intermediate **6** to **8** and from **10** to **12**. This completely parallel series of steps (not shown) likewise serves to move the benzene ring in **6** from the *β*-position on the naphthalene ring system to the α-position (also by way of **8**, **9**, and **10**), leading ultimately to fluoranthene (**3**).

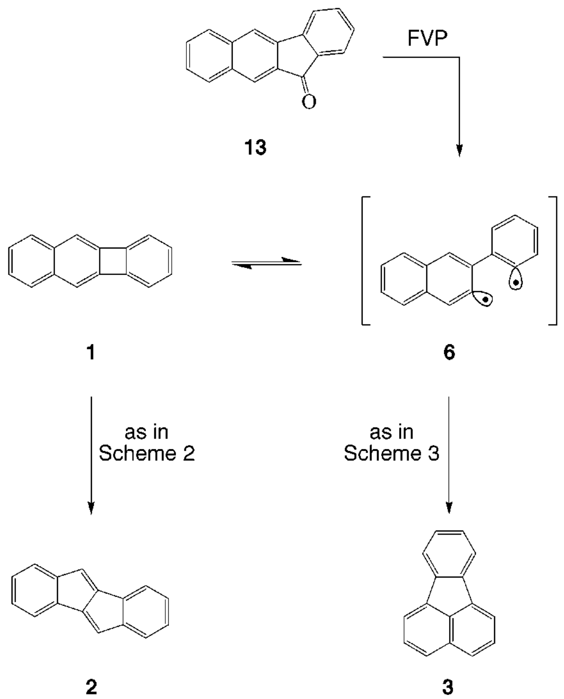
This mechanistic picture suggests that independent generation of diradical **6** from another precursor might yield a proportion of fluoranthene (**3**), relative to indeno[2,1-*a*]indene (**2**), higher than that obtained from the FVP of **1**. In accord with this prediction, we have found that FVP of benzo[*b*]fluorenone (**13**)[13,14] affords fluoranthene (**3**) as a major product at both 900 and 1100 °C (Scheme 4). Thus, a significant fraction of the initial diradical (**6**) formed by decarbonylation of **13** goes on to fluoranthene directly (Scheme 4); the remainder cyclizes to benzo[*b*]biphenylene (**1**), which then rearranges according to the partitioning reported above (Scheme 1).

Not surprisingly, in light of the results presented above, FVP of 5,12-naphthacene quinone (**14**)[15,16] affords fluoranthene (**3**) as the dominant product at both temperatures (900 and 1100 °C) and gives only small amounts of indeno[2,1-

Scheme 3

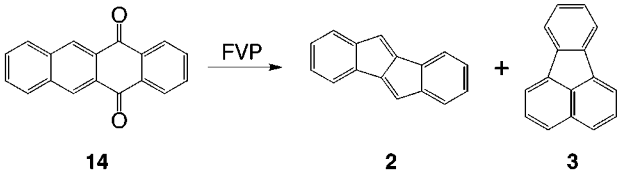


Scheme 4



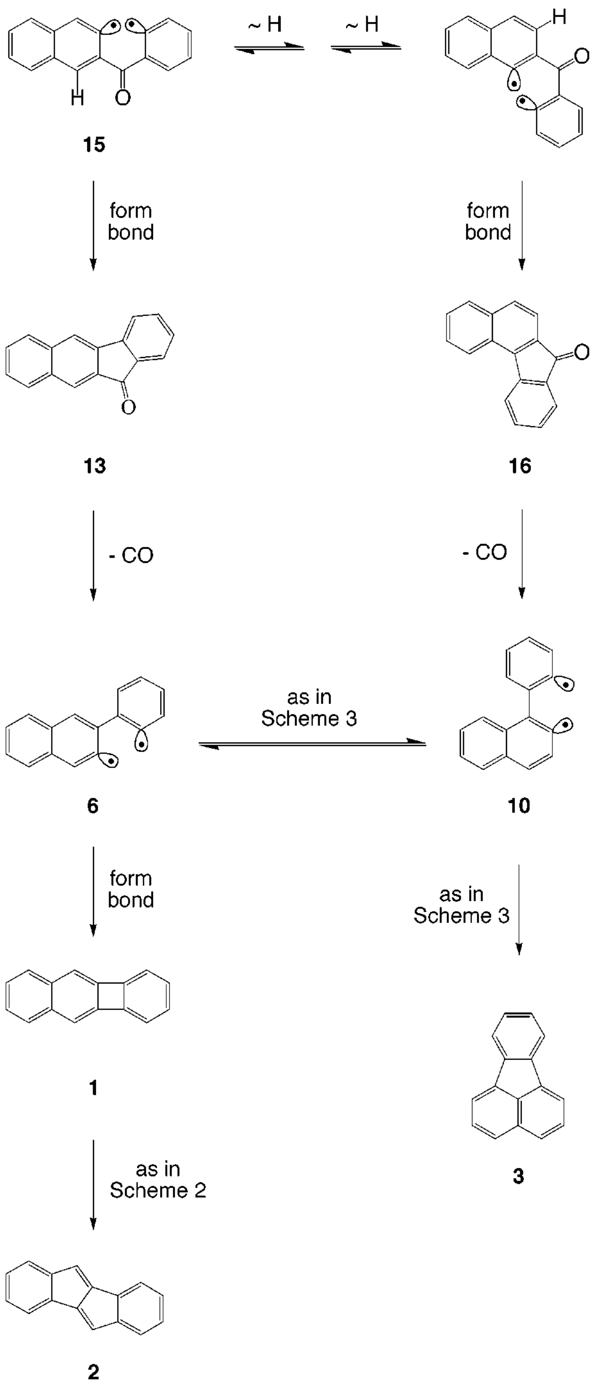
Temperature (°C)	Product Ratio (**2** : **3**)
900	5 : 5
1100	2 : 8

Scheme 5



Temperature (°C)	Product Ratio (**2** : **3**)
900	2 : 8
1100	1 : 9

Scheme 6



a]indene (**2**) (Scheme 5). A portion of the diradical formed by the initial decarbonylation in this case (**15**) presumably cyclizes to benzo[*b*]fluorenone (**13**), which then yields products **2** and **3** in the ratios reported in Scheme 4. The shift in the product distribution toward fluoranthene (**3**), however, suggests that a significant fraction of **15** must be cyclizing to benzo[*c*]fluorenone (**16**) (Scheme 6). Decarbonylation of **16** would generate diradical **10**, an intermediate in Scheme 3 that is well on its way to fluoranthene (**3**), which could isomerize to **2** only by going all the way back to benzo[*b*]biphenylene (**1**).

In conclusion, we have studied new transformations that occur on the $C_{16}H_{10}$ energy surface at high temperatures. Our

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(3) Flash vacuum pyrolyses (FVPs) were performed on 100 mg samples of compound **1** with a steady flow of nitrogen carrier gas as previously described.[4] At 900 °C, the mass recovery was 75% (75 mg), whereas at 1100 °C, the mass recovery was 70% (70 mg). Approximately 30−35% of unchanged **1** was recovered from the 900 °C pyrolysis, but none survives in the 1100 °C pyrolysis.

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(5) The product ratio (**2**:**3**) was determined by ^{1}H NMR spectroscopic analysis of the crude product mixture. At 1100 °C, fluoranthene equilibrates with acephenanthrylene by the well-known benzene ring contraction rearrangement (“5/6 ring-switch”).[6] The numbers reported for fluoranthene (**3**) at 1100 °C therefore represent the sum of the concentrations of fluoranthene and acephenanthrylene.

results provide one of the simplest examples imaginable of a phenyl group migration around the perimeter of a dehydro-PAH (in this case, dehydronaphthalene). Such a process may well play a role in the formation of large PAHs, fullerenes, soot, and other carbonaceous material during the combustion or pyrolysis of low molecular weight hydrocarbons and fossil fuels.[17] More specifically, it could play a major role in the formation of nonalternant PAHs at high temperatures from oxygenated precursors, such as ketones and/or quinones. The thermal generation of nonalternant hydrocarbons from alternant hydrocarbons is not unprecedented,[7,18] but we know of no prior examples that involve phenyl migrations of the sort described here.[19]

Acknowledgment. We thank the Department of Energy for financial support of this work.

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(6) (a) Scott, L. T.; Roelofs, N. H. *J. Am. Chem. Soc.* **1987**, *109*, 5461−5. (b) Scott, L. T.; Roelofs, N. H. *Tetrahedron Lett.* **1988**, *29*, 6857−60. (c) Anderson, M. R.; Brown, R. F. C.; Coulston, K. J.; Eastwood, F. W.; Ward, A. *Aust. J. Chem.* **1990**, *43*, 1137−50. (d) Brown, R. F. C.; Eastwood, F. W.; Wong, N. R. *Tetrahedron Lett.* **1993**, *34*, 3607−8.

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(8) Scott, L. T.; Hashemi, M. M.; Schultz, T. H.; Wallace, M. B. *J. Am. Chem. Soc.* **1991**, *113*, 9692−3.

(9) For examples of other high-temperature reactions that appear to involve homolytic cleavage of strained sp^2-sp^2 carbon−carbon single bonds, see: (a) Sarobe, M.; Kwint, H. C.; Fleer, T.; Jenneskens, L. W.; Wesseling, J. *Tetrahedron Lett.* **1998**, *39*, 9823−6. (b) Sarobe, M.; Kwint, H. C.; Fleer, T.; Hevenith, R. W. A.; Jenneskens, L. W.; Vlietstra, E. J.; Van Lenthe, J. H.; Wesseling, J. *Eur. J. Org. Chem.* **1999**, 1191−1200.

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(12) Cioslowski, J.; Liu, G.; Moncrieff, D. *J. Org. Chem.* **1996**, *61*, 4111−4.

(13) Latif, A.; Soliman, G. *J. Chem. Soc.* **1944**, 56−8.

(14) FVPs were performed on 300 mg samples of compound **13** with a steady flow of nitrogen carrier gas as previously described.[4] At 900 °C, the mass recovery was 45% (120 mg), whereas at 1100 °C, the mass recovery was 38% (100 mg).[5]

(15) Purchased from Aldrich Chemical Co.

(16) FVPs were performed on 1000 mg samples of compound **14** with a steady flow of nitrogen carrier gas as previously described.[4] At 900 °C, the mass recovery was 47% (370 mg), whereas at 1100 °C, the mass recovery was 43% (340 mg).[5]

(17) See, for example: (a) Howard, J. B.; Lafleur, A. L.; Makarovsky, Y.; Mitra, S.; Pope, C. J.; Yadav, T. K. *Carbon* **1992**, *30*, 1183−201. (b) Ahrens, J.; Bachmann, M.; Baum, T.; Griesheimer, J.; Kovacs, R.; Weilmuenster, P.; Homann, K. H. *Int. J. Mass Spectrom. Ion Processes* **1994**, *138*, 133−48. (c) Homann, K.-H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2435−51. (d) Richter, H.; Grieco, W. J.; Howard, J. B. *Chem. Phys. Processes Combust.* **1997**, 135−138. (e) Richter, H.; Grieco, W. J.; Howard, J. B. *Combust. Flame* **1999**, *119*, 1−22. (f) Marr, L. C.; Kirchstetter, T. W.; Harley, R. A.; Miguel, A. H.; Hering, S. V.; Hammond, S. K. *Environ. Sci. Technol.* **1999**, *33*, 3091−9.

(18) (a) Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291−300. (b) Neilen, R. H. G.; Wiersum, U. E. *Chem. Commun.* **1996**, 149−50. (c) Sarobe, M.; Jenneskens, L. W.; Wiersum, U. E. *Tetrahedron Lett.* **1996**, *37*, 1121−2. (d) Matzger, A. J.; Vollhardt, K. P. C. *Chem. Commun.* **1997**, 1415−6. (e) Necula, A.; Scott, L. T. *J. Anal. Appl. Pyrolysis* **2000**, *54*, 65−87.

(19) For acid-catalyzed phenyl group migrations around the perimeter of aromatic hydrocarbons, see: Necula, A.; Racoveanu-Schiketanz, A.; Gheorghiu, M. D.; Scott, L. T. *J. Org. Chem.* **1995**, *60*, 3448−51 and references therein.