1,2-Shifts of Hydrogen Atoms in Aryl Radicals

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Abstract: An energy barrier on the order of 60 kcal/mol is predicted for the 1,2-shift of hydrogen atoms in aryl radicals. Such rearrangements are, therefore, not expected to occur under ordinary laboratory conditions, but they should be prevalent in the aryl radicals formed during combustion, flash vacuum pyrolysis, and other high-temperature gas-phase processes. As a demonstration of this rearrangement, the 2-benzo[*c*]phenanthryl radical (**1**) was generated by flash vacuum pyrolysis of the corresponding aryl bromide (**9**). A 1,2-shift of hydrogen out of the sterically congested cove region of **1**, followed by cyclization and rearomatization of the resulting radical (Scheme 1), is proposed to explain the observation of benzo[*ghi*]fluoranthene (**4**) as the dominant monomeric product formed. Under the same conditions, [1,3,4,5-^{2}H$_4$]-2-bromobenzo[*c*]phenanthrene (**13**) gives [1,2,3,4-^{2}H$_4$]-benzo[*ghi*]fluoranthene (**15**) as the dominant monomeric product (Scheme 6), in accord with the expectation of a deuterium atom 1,2-shift.

Every chemist has heard of the 1,2-shifts of hydrogen atoms and alkyl groups (Wagner−Meerwein rearrangements) that pervade the chemistry of carbocations,[1−3] but few know much about the analogous rearrangements of organic free radicals[4−6] and carbanions.[7−10] Examples of the latter processes, in fact, are comparatively rare, and in those cases where they do appear to occur, nonconcerted mechanisms frequently prevail.[11−14]

A satisfying explanation for the special proclivity of carbocations for 1,2-shift rearrangements, and for the reluctance of radicals and carbanions to behave similarly, can be found in the Woodward−Hoffmann rules of orbital symmetry conservation. Such rearrangements are properly viewed as pericyclic transformations (i.e., [1,2] sigmatropic reactions) that proceed by way of three-centered transition states involving the cyclic delocalization of two electrons for cations, three electrons for radicals, and four electrons for carbanions. Thus, 1,2-shift rearrangements in cations involve *aromatic* transition states (4*N* + 2 electrons in the cycle), which makes them "symmetry allowed", whereas the same rearrangements in carbanions would involve *antiaromatic* transition states, which makes them "symmetry forbidden". The transition states for 1,2-shift rearrangements in radicals are neither strongly stabilized by aromaticity nor strongly destabilized by antiaromaticity; therefore, the activation energies for such process should be large, but not necessarily prohibitively so. A simple computational analysis (next section) suggests that aryl radicals should be good candidates to exhibit 1,2-shift rearrangements of hydrogen atoms.

Computational Results

For calculations involving the energies of aryl radicals, density functional theory has proven superior to conventional unrestricted Hartree−Fock theory and gives results that agree quite well with experiment.[15,16] BLYP/6-311G** calculations (corrected for zero-point vibrational energy, ZPE, differences), for example, give a value of 106.9 kcal/mol for the homolytic C−H bond dissociation energy of benzene,[16] which compares favorably with the recently reported experimental values of 109.8 ± 0.8 kcal/mol[17] and 112.0 ± 0.6 kcal/mol.[18] We obtained a value of 109.4 kcal/mol for the homolytic C−H bond dissociation energy of benzene using BP/DN** density functional calculations[19] (ZPE-corrected) and have performed the calculations below at this level of theory.

In vinyl radical, the activation energy calculated for a 1,2-shift of hydrogen (43.5 kcal/mol) actually exceeds the energy

(1) For a review on 1,2-shifts in carbocations, see: Vogel, P. *Carbocation Chemistry*; Elsevier: New York, 1985; pp 323−372.

(2) See also: Shubin, V. G. *Top. Curr. Chem.* **1984**, *116/117*, 267−341.

(3) See also: Kirmse, W. *Top. Curr. Chem.* **1979**, *80*, 89−124.

(4) For a review on 1,2-shifts in radicals, see: Wilt, J. W. *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I., p 333−501.

(5) See also: Nonhebel; Walton *Free-Radical Chemistry*; Cambridge University Press: London, 1974; pp 498−552.

(6) See also: Friedlina, R. K. *Adv. Free Radical Chem.* **1965**, *1*, 211.

(7) For a review on 1,2-shifts in carbanions, see: Zimmerman, H. E. *Molecular Rearrangements*, Part 1; de Mayo, P., Ed.; Wiley: New York, 1963; p 345.

(8) See also: Cram, D. J. *Fundamentals of Carbanion Chemistry*; Academic Press: New York, 1965; Chapter VI.

(9) See also: Buncel, E. *Carbanions: Mechanistic and Isotopic Aspects*; Elsevier: Amsterdam, 1975.

(10) See also: Hunter, D. H.; Stothers, J. B. *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, p 392.

(11) For a review on the Stevens rearrangement, see: Lepley, A. R.; Giumanini, A. G. *Mech. Mol. Migr.* **1971**, *3*, 297−440.

(12) See also: Pine, S. H. *Org. React.* **1970**, *18*, 403−464.

(13) For a review on the Wittig rearrangement, see: Johnstone, R. A. W. *Mech. Mol. Migr.* **1969**, *2*, 249−266.

(14) For reviews on neophyl rearrangements, see refs 4−6.

(15) Barone, V.; Adamo, C.; Russo, N. *Int. J. Quantum Chem.* **1994**, *52*, 963−971.

(16) Cioslowski, J.; Liu, G.; Martinov, M.; Piskorz, P.; Moncrieff, D. *J. Am. Chem. Soc.* **1996**, *118*, 5261−5264.

(17) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744−2765.

(18) Davico, G. E.; Bierbaum, V. M.; DePuy, C. H.; Ellison, G. B.; Squires, R. R. *J. Am. Chem. Soc.* **1995**, *117*, 2590−2599.

(19) BP/DN** calculations were performed using the density functional program implemented in the Spartan 5.0 software package (Wavefunction, Inc., Irvine, CA 92612). Vibrational analyses at the BP/DN** level of theory have confirmed that the transition-state species reported here are characterized by one and only one imaginary vibrational frequency and that species corresponding to energy minima have no imaginary vibrational frequencies.
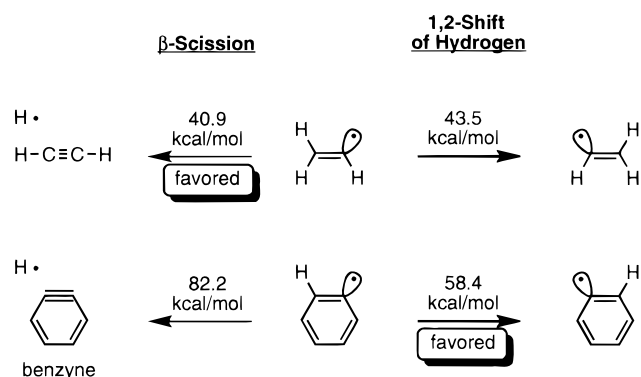
Figure 1. Energy required for β-scission and for 1,2-shift of hydrogen in the vinyl radical (top) and phenyl radical (bottom). All calculations performed at the BP/DN** level of theory[19] and corrected for zero-point vibrational energy (ZPE) differences.

required for simple β-scission to give acetylene and a hydrogen atom (40.9 kcal/mol) at the BP/DN** level of theory (both values ZPE-corrected). Wang et al. have reached the same conclusion using electron correlated ab initio computational methods.[20] In phenyl radical, on the other hand, β-scission should be strongly disfavored, owing to the high strain energy of the benzyne that would be generated. Indeed, we find the calculated activation energy for a 1,2-shift of hydrogen in phenyl radical (58.4 kcal/mol) to be considerably less than the energy required for β-scission (82.2 kcal/mol) at the BP/DN** level of theory (both values ZPE-corrected).[21,22] Figure 1 summarizes these computational results.

Clearly, hydrogen atom 1,2-shifts in aryl radicals must be far less favorable energetically than the familiar [1,2]-sigmatropic rearrangements of carbocations, and they certainly would not be expected to occur spontaneously under ordinary laboratory conditions. We are unaware of any prior examples, other than our own, and herein offer what we believe to be the first closely examined case.[23-26]

System Design

The rather substantial activation energy predicted by the above calculations for a 1,2-shift of hydrogen in the phenyl radical persuaded us that it would be prudent to design a system wherein (a) the 1,2-shift of hydrogen could benefit from some thermodynamic driving force and (b) a diagnostic reaction channel

(20) Coupled cluster ab initio calculations corrected for electron correlation, using Dunning's triple-ζ polarization basis set (CCSD(T)/TZ2P), as implemented in the ACES II program, give an activation energy of "at least 47 kcal/mol" for the 1,2-shift of hydrogen in vinyl radical and a dissociation threshold of 40.7 kcal/mol for the β-scission of vinyl radical to acetylene and a hydrogen atom: Wang, J.-H.; Chang, H.-C.; Chen, Y.-T. *Chem. Phys.* **1996**, *206*, 43−56.

(21) The only prior calculations we have found for the 1,2-shift of hydrogen in phenyl radical, although now quite out of date, also predicted a high energy barrier: Burmistrov, V. N.; Khudyakov, I. V.; Christensen, A. *Izv. Akad. Nauk, Ser. Khim.* **1979**, 460−2 (*Chem. Abstr.* No. 90:186104).

(22) See also van der Hart, W. J. *J. Am. Soc. Mass Spectrom.* **1995**, *6*, 513−5.

(23) Evidence for the migration of hydrogen atoms in dehydrobenzenes (aryl *di*radicals) at elevated temperatures has been seen in the beautiful work of R. F. C. Brown et al.: Brown, R. F. C.; Eastwood, F. W. *Pure Appl. Chem.* **1996**, *68*, 261−266.

(24) See also: Banciu, M. D.; Brown, R. F. C.; Coulston, K. J.; Eastwood, F. W.; Jurss, C.; Mavropoulos, I.; Stanescu, M.; Wiersum, U. E. *Aust. J. Chem.* **1996**, *49*, 965−976.
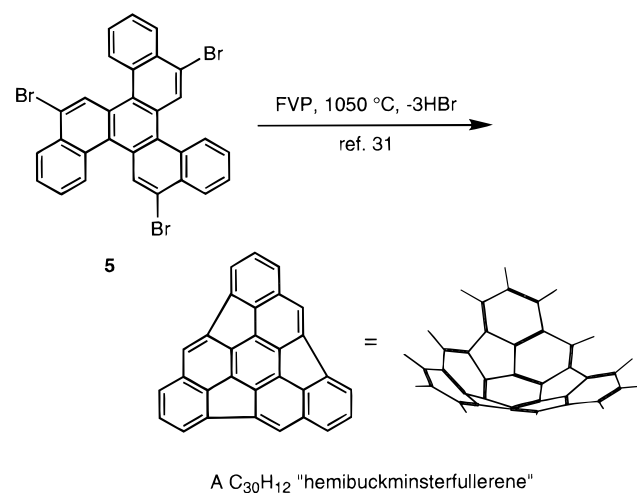
(25) See also: Bapat, J. B.; Brown, R. F. C.; Bulmer, G. H.; Childs, T.; Coulston, K. J.; Eastwood, F. W.; Taylor, D. K. *Aust. J. Chem.* **1997**, *50*, 1159−1182.

(26) See also: Brown, R. F. C.; Coulston, K. J.; Eastwood, F. W. *Aust. J. Chem.* **1997**, *50*, 1183−1189.

Scheme 1

Scheme 2

A C$_{30}$H$_{12}$ "hemibuckminsterfullerene"
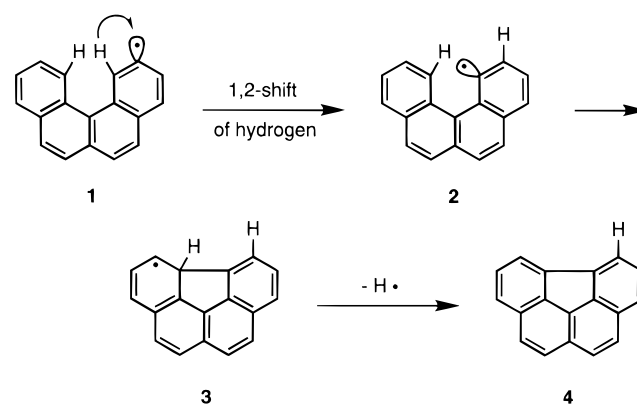
would be made available to the newly created aryl radical only after the hydrogen has shifted.

The 2-benzo[*c*]phenanthryl radical (**1**) offers both of these features. To begin with, a 1,2-shift of hydrogen out of the cove region to the adjacent radical center ought to be accompanied by a significant relief of steric congestion. We calculate an exothermicity of 5.3 kcal/mol for this rearrangement at the BP/DN** level of theory (ZPE-corrected).[27] Equally importantly, following the 1,2-shift of hydrogen, the new aryl radical suddenly gains access to an irreversible cyclization reaction (**2** → **3** → **4**, Scheme 1).

To generate aryl radical **1** under conditions that would give it enough energy to surmount a barrier of nearly 60 kcal/mol, we decided to subject the corresponding aryl bromide (**9**) to flash vacuum pyrolysis. The C−Br homolytic bond dissociation energy of bromobenzene is 82.7 ± 1.1 kcal/mol,[17] and thus any temperature that is sufficient to rupture the C−Br bond in **9** should provide more than enough energy to promote the subsequent 1,2-shift of hydrogen, assuming our calculations are correct. The pyrolysis of aryl bromides has been used for many years as a classic means of generating aryl radicals in the gas phase.[28-30]
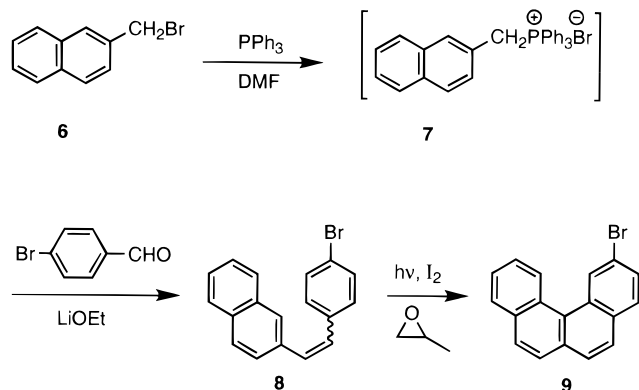
(27) Cioslowski et al. have calculated an exothermicity of 6.9 kcal/mol for the difference in energy between **1** and **2** at the BLYP/6-311G** level of theory (ZPE corrected).[16]

(28) Ladaki, M.; Szwarc, M. *J. Chem. Phys.* **1952**, *20*, 1814.

(29) Ladaki, M.; Szwarc, M. *Proc. R. Soc. London, Ser. A* **1953**, *A219*, 341.

(30) Benson, S. W.; O'Neal, H. E. *Kinetic Data on Gas-Phase Unimolecular Reactions;* NBS-NSRDS 21, U.S. Government Printing Office: Washington, DC, 1970.

Scheme 3

Syntheses of Aryl Radical Precursors

Although the requisite 2-bromobenzo[*c*]phenanthrene (**9**) had been synthesized before,[32] we developed the convenient, alternative, two-pot synthesis illustrated in Scheme 3. Thus, a solution of the commercially available 2-bromomethylnaphthalene (**6**) and triphenylphosphine in dimethylformamide was heated to reflux to form the phosphonium salt (**7**). This intermediate was not isolated but was used in situ for a Wittig reaction by first cooling the solution to room temperature and then adding *p*-bromobenzaldehyde and lithium ethoxide. Chromatographic separation of the cis and trans product isomers, although possible, was found to be unnecessary, since the isomers interconvert photochemically in the next step. Photocyclization of the mixture of stilbenes (**8**) in the presence of propylene oxide[33] gave 2-bromobenzo[*c*]phenanthrene (**9**).[32]

As described in the next section, pyrolysis of **9** does indeed give benzo[*ghi*]fluoranthene (**4**), the product expected from the aryl radical generated by a 1,2-shift of hydrogen out of the cove region (Scheme 1). We therefore prepared an isotopically labeled derivative of **9** to see whether a deuterium in the cove region would migrate to the site of the initial radical. Synthesis of the deuterated analogue **13** was achieved by replacing *p*-bromobenzaldehyde in Scheme 3 with *p*-bromobenzaldehyde-d_5 (**12**, Scheme 4). The extra ("spectator") deuterium atoms at positions 3, 4, and 5 in **13** that result from this synthetic strategy are not involved in the hydrogen shift and thus do not affect the results.

As summarized in Scheme 4, the synthetic route to **13** began with bromination of toluene-d_8 in trifluoroacetic acid-d_1.[34]
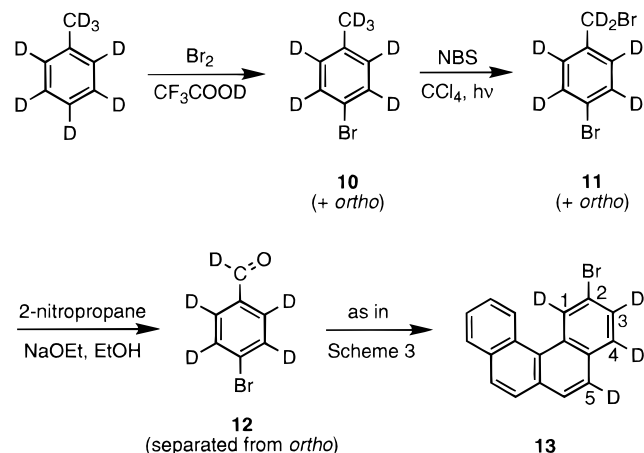
(31) Hagen, S.; Bratcher, M. S.; Erickson, M. S.; Zimmermann, G.; Scott, L. T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 406−408.
(32) Martin, R. H.; Moriau, J.; Defay, N. *Tetrahedron* **1974**, *30*, 179−185.
(33) Liu, L.; Yang, B.; Katz, T. J.; Poindexter, M. K. *J. Org. Chem.* **1991**, *56*, 3769−3775.
(34) Brown, H. C.; Wirkkala, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 1447−1452.

Scheme 4

Removal of the minor quantity of unwanted ortho-isomer turned out to be easier at a later stage in the reaction sequence, and thus the impure *p*-bromotoluene-d_7 (**10**) was treated directly with *N*-bromosuccinimide in refluxing carbon tetrachloride to give *p*-bromobenzyl bromide-d_6 (**11**), contaminated by a small quantity of the ortho-isomer. Oxidation of this mixture with the sodium salt of 2-nitropropane in ethanol[35−38] gave the desired *p*-bromobenzaldehyde-d_5 (**12**), which was separated from the ortho-isomer by chromatography. Wittig coupling of **12** with the ylide derived from phosphonium salt **7** followed by photolysis as before gave [1,3,4,5-^{2}H$_4$]-2-bromobenzo[*c*]phenanthrene (**13**).

Pyrolysis Results and Discussion

Flash vacuum pyrolyses were performed on 50-mg samples of 2-bromobenzo[*c*]phenanthrene (**9**) at temperatures ranging from 950 to 1100 °C, with a controlled influx of nitrogen to serve as a carrier gas (final pressure = 2.0−2.5 mmHg). The product mixture consisted of unchanged **9**, benzo[*ghi*]fluoranthene (**4**),[39−41] and benzo[*c*]phenanthrene (**14**)[32,42−45] (Scheme 5). The composition of the product mixture was determined by ^{1}H NMR analysis and was found to vary with the pyrolysis temperature (Table 1).

The presence of benzo[*c*]phenanthrene (**14**) as a minor product in the pyrolysates reflects the well-known fact[46,47] that aryl radicals (**1** and **2** in this reaction) are capable of abstracting hydrogen atoms from other organic species in the gas phase or on the walls of the pyrolysis tube. At 950 °C the product formed by what appears to involve a hydrogen shift (**4**) outweighs the product formed by hydrogen abstraction (**14**) by a factor of 25:6

(35) Modification of the method by Hass, H. B.; Bender, M. L. *J. Am. Chem. Soc.* **1949**, *71*, 1767−1769.
(36) See also: Hass, H. B.; Bender, M. L. In *Organic Syntheses;* Rabjohn, N., Ed.; 1963, Collect. Vol. 4, pp 932−934.
(37) See also: Yamamoto, K.; Ikeda, T.; Kitsuki, T.; Okamoto, Y.; Chikamatsu, H.; Nakazaki, M. *J. Chem Soc., Perkin Trans. 1* **1990**, 271−276.
(38) See also: Yamamoto, K.; Sonobe, H.; Matsubara, H.; Sato, M.; Okamoto, S.; Kitaura, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 69−70.
(39) Campbell, R.; Reid, D. H. *J. Chem. Soc.* **1952**, 3281−3284.
(40) Crombie, D. A.; Shaw, S. *J. Chem. Soc.* **1969**, 2489−2490.
(41) Studt, P.; Win, T. *Liebigs Ann. Chem.* **1983**, 519.
(42) Cook, J. W. *J. Chem. Soc.* **1931**, 2525−2529.
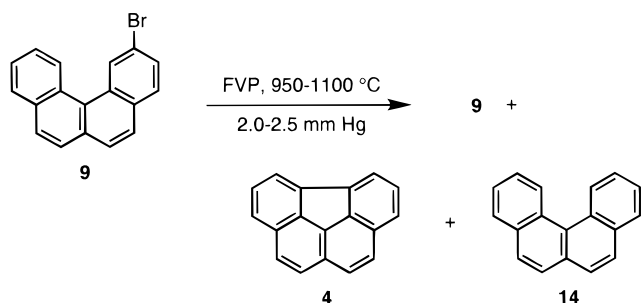(43) Szmuszkovicz, J.; Modest, E. J. *J. Am. Chem. Soc.* **1948**, *70*, 2542−2543.
(44) Defay, N.; Zimmermann, D.; Martin, R. H. *Tetrahedron Lett.* **1971**, *21*, 1871−1874.
(45) Pataki, J.; Harvey, R. G. *J. Org. Chem.* **1982**, *47*, 20−22.
(46) Fahr, A.; Stein, S. E. *J. Phys. Chem.* **1988**, *92*, 4951−4955.
(47) Chen, R. H.; Kafafi, S. A.; Stein, S. E. *J. Am. Chem. Soc.* **1989**, *111*, 1418−1423.

Before describing the experimental aspects of the present project, it is relevant to note a prior discovery in our lab. Heartened only by a hunch that the chemistry depicted in Scheme 1 should work, but with no experimental precedent, we developed an efficient synthesis of tribromobenzo[*c*]naphtho-[2,1-*p*]chrysene (**5**) and subjected it to flash vacuum pyrolysis at 1050 °C. As we had hoped, the C−Br bonds were broken, and that initiated what appears to be a 3-fold version of the cyclization reaction proposed in Scheme 1, giving us a marvelous, bowl-shaped, C_3-symmetric $C_{30}H_{12}$ "hemibuckminsterfullerene" (Scheme 2).[31] A desire to understand more thoroughly the details of this remarkable transformation was, in fact, our motivation for the present project.

Scheme 5

Table 1. Flash Vacuum Pyrolyses of 2-Bromobenzo[*c*]phenanthrene (**9**)

| temp (°C)	mass recovery (%)[b]	relative amounts[a]			yield of purified mixture (%)
		9 (%)	**4** (%)	**14** (%)	
950	72	69	25	6	37
1000	73	31	60	9	27
1050	97	0	90	10	35
1100	86	0	90	10	29

[a] Determined by integration of the ^{1}H NMR spectra of the purified mixture of monomeric products; error limits estimated at approximately ±5%. [b] Mass recovery (%) based on the theoretical yield of **4**.
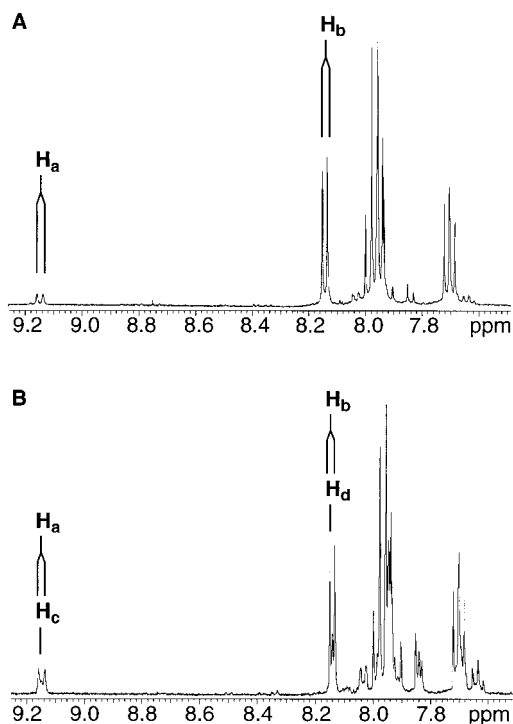
Figure 2. ^{1}H NMR spectra of the pyrolysate from FVP of (**A**) 2-bromobenzo[*c*]-phenanthrene and (**B**) [1,3,4,5-^{2}H$_4$]-2-bromobenzo-[*c*]phenanthrene.

or about 4:1 (Table 1). As the temperature is raised, the hydrogen-shift pathway grows increasingly dominant (ca. 7:1 at 1000 °C and 9:1 at 1050 and 1100 °C).

Figure 2A shows the ^{1}H NMR spectrum of the product mixture obtained from pyrolysis of 2-bromobenzo[*c*]phenanthrene (**9**) at 1050 °C. The small doublet at 9.15 ppm (labeled H$_a$) comes from the hydrogen in the cove region of the minor product (**14**), whereas the large doublet at 8.14 ppm (labeled H$_b$) comes from the hydrogen in the five-membered ring bay region of the major product (**4**), i.e., the hydrogen shown explicitly on the structure of **4** in Scheme 1. The dominance of the hydrogen-shift pathway is clearly apparent.

Scheme 6
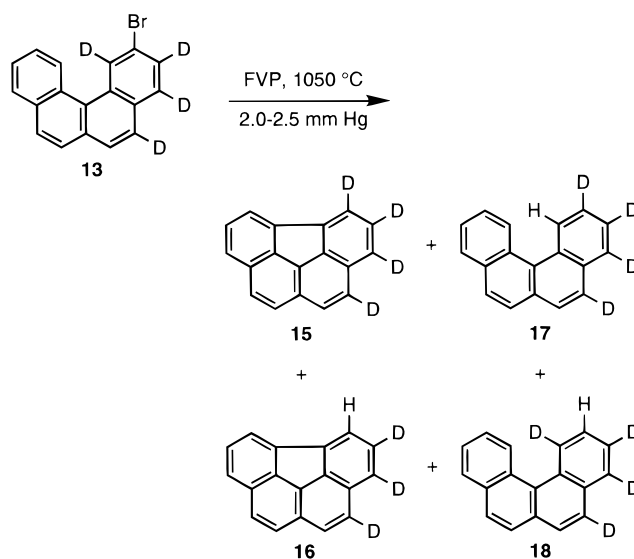
Since the optimum temperature for ring closure of **9** to **4** was found to be 1050 °C (Table 1), pyrolysis of the deuterated analogue (**13**) was likewise performed at 1050 °C under the same conditions (Scheme 6). ^{1}H NMR analysis of the pyrolysate (Figure 2B) indicates that the products of cyclization (**15** + **16**) again outweigh the products of hydrogen abstraction (**17** + **18**), although now in a ratio of only approximately 3:1. No starting material (**13**) survived. The reduced dominance of the hydrogen-shift pathway is consistent with an unfavorable kinetic isotope effect, which could retard the deuterium 1,2-shift but should not affect the rate of the hydrogen-abstraction reactions leading to **17** and **18**.

Comparing the ^{1}H NMR spectrum of the pyrolysate from **13** (Figure 2B) with that from the pyrolysis of the nondeuterated aryl bromide (**9**, Figure 2A), we see a new, small singlet in the trough of the original doublet at 9.15 ppm (labeled H$_c$ and H$_a$, respectively, in Figure 2B). This signal comes from a hydrogen in the cove region of a benzo[*c*]phenanthrene that must have a deuterium at the adjacent position, since it lacks vicinal coupling. We assign that singlet to compound **17**, which presumably is formed by a 1,2-shift of deuterium followed by a hydrogen abstraction. Compound **17** should also contribute to the doublet at 9.15 ppm (labeled H$_a$), since the other hydrogen in the cove region of **17** does have a hydrogen neighbor.

The fact that doublet H$_a$ in Figure 2B is larger than singlet H$_c$, however, indicates that another compound must also contribute to the doublet labeled H$_a$. The logical candidate is **18**, the expected product of hydrogen abstraction by the original aryl radical, prior to any 1,2-shift of deuterium. The singlet for the hydrogen in **18** attached to the position vacated by the bromine atom, unfortunately, is lost among the jumble of signals at higher field. From the signals at 9.15 ppm, therefore, we conclude that both **17** and **18** were formed; however, the signals are small, and thus both are just minor products.

Following a 1,2-shift of deuterium, the newly formed radical in the cove region has a choice between hydrogen abstraction to give **17** (already identified above) and cyclization to give **15**. Recalling the dominance of cyclization over hydrogen abstraction in the nondeuterated radicals (Figure 2A), we would expect **15** to be formed in greater amount than **17**, and such appears to be the case. Compound **15** is responsible for the major portion of the large doublet at 8.14 ppm (labeled H$_b$ in Figure 2B). The other contribution to the doublet labeled H$_b$ in Figure

Scheme 7
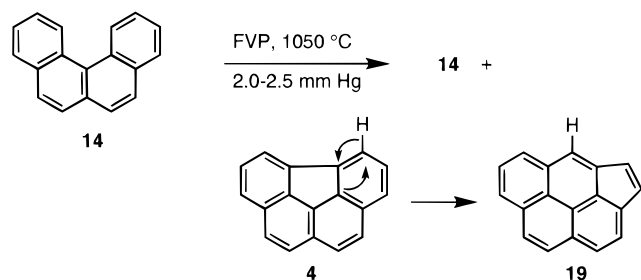
2B is compound **16**, the presence of which is revealed by the small singlet at 8.14 ppm labeled H_d. Although the pathway by which **16** is formed may not be obvious (discussed further below), it should be recognized that **16** is a minor product relative to **15**, as are **17** and **18**. The most important conclusion, therefore, is that *the single most abundant product (**15**) and one of the three minor products (**17**) from the pyrolysis of **13** are those expected from a 1,2-shift of deuterium.*

The minor cyclized product **16**, which has no deuterium at the site where bromine was originally attached, most likely represents a secondary product, formed by cyclodehydrogenation of **18**. Pyrolysis of benzo[*c*]phenanthrene (**14**) is known to give benzo[*ghi*]fluoranthene (**4**), usually accompanied by varying amounts of the subsequent rearrangement product cyclopenta-[*cd*]pyrene (**19**), depending on the temperature and the pressure (Scheme 7).[48−50]

Under our conditions (1050 °C, nitrogen carrier gas, pressure = 2.0−2.5 mmHg), the pyrolysis of **14** gives mostly unchanged **14** (78%) plus minor amounts of **4** (12%) and **19** (10%).[51,52] This degree of conversion establishes a lower limit of what would be seen during the pyrolysis of aryl bromides **9** and **13**, since the substantially higher concentrations of aryl radicals in those experiments should promote the cyclodehydrogenation of benzo[*c*]phenanthrene by exothermic hydrogen-atom abstraction from the cove region. The unimolecular isomerization of **4** to **19**, on the other hand, should remain relatively insignificant, which presumably accounts for why we see none from the pyrolysis of aryl bromides **9** and **13**.

The alternative possibility that **16** might be formed from **13** by way of the benzyne intermediate **20** (Scheme 8) looks attractive on the surface, but our results exclude this pathway. Precedent abounds for the reversible ring contraction of benzynes and for subsequent trapping of the resulting vinylidenes by C−H bond insertion;[23−26,53] however, the final 6/5-ring switch rearrangement required to generate **16** from **22** would be endothermic; cyclopenta[*cd*]pyrene is known to be the energy sink on the $C_{18}H_{10}$ energy surface.[48−50] The absence of any detectable **22** among the pyrolysis products from **13** argues against this benzyne mechanism as the source of **16**.

Conclusion

From an aryl radical poised to relieve steric congestion by a 1,2-shift of hydrogen (**1**), the dominant product (**4**) has been found to derive from the rearranged radical. Deuterium-labeling

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(49) Plater, M. J. *Tetrahedron Lett.* **1994**, *35*, 6147−6150.
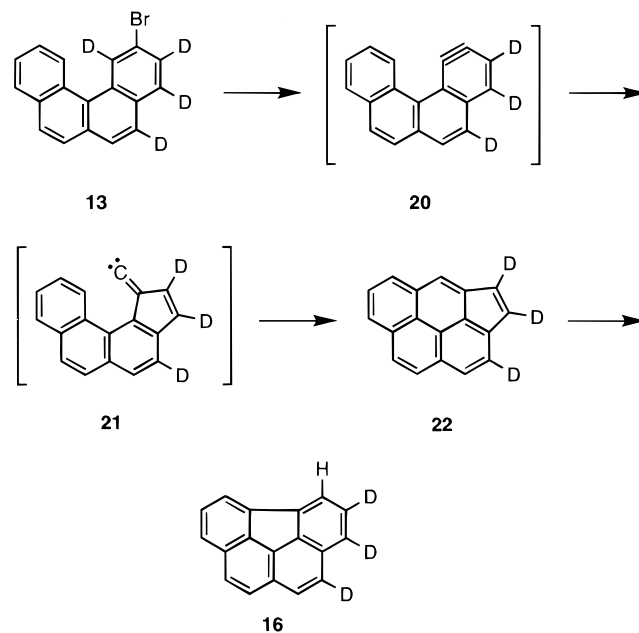(50) Sarobe, M.; Jenneskens, L. W.; Wiersum, U. E. *Tetrahedron Lett.* **1996**, *37*, 1121−1122.
(51) Tintel, C.; Cornelisse, J.; Lugtenburg, J. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 14−20.
(52) Jans, A. W. H.; Tintel, C.; Cornelisse, J.; Lugtenburg, J. *Magn. Reson. Chem.* **1986**, *24*, 101−104.
(53) Brown, R. F. C.; Eastwood, F. W. *Synlett* **1993**, 9−19 and references therein.

Scheme 8

studies provide further evidence that the major reaction pathway involves migration of an adjacent hydrogen atom to the site where the original radical was generated. The high temperatures employed to induce homolytic cleavage of an aryl bromide bond (flash vacuum pyrolysis at 950−1100 °C) gives the resulting radical more than enough energy to surmount the barrier for hydrogen migration. These results strongly suggest that the 1,2-shift of hydrogen atoms at high temperatures should also occur in simple aryl radicals, such as the phenyl radical, for which an energy barrier of 58.4 kcal/mol has been calculated.

Aryl radicals are believed to play a major role in the chemistry of flames, combustion, and soot formation. Kinetic models for such processes should take into account the intramolecular equilibrations of isomeric radicals, such as the 1- and 2-naphthyl radicals, by reversible 1,2-shifts of hydrogens atoms.

Experimental Section

General. Diethyl ether was purified by distillation under nitrogen from the sodium ketyl of benzophenone. All other solvents and commercial chemicals were of the best available grade and were used without further purification, unless otherwise stated. Proton NMR chemical shifts are reported in ppm downfield from tetramethylsilane with tetramethylsilane (δ = 0.00 ppm) as the reference standard, unless otherwise specified. Carbon NMR shifts are reported in ppm downfield from tetramethylsilane with deuteriochloroform (δ = 77.23 ppm) as the reference standard. Preparative thin layer chromatographies were performed on 20 cm × 20 cm Analtech Uniplate Taper plates, silica gel GF. For column chromatographies, silica gel 60−200 mesh was used. High-resolution mass spectrometry (HRMS) was performed by the Mass Spectroscopy Laboratory, School of Chemical Sciences, University of Illinois. Elemental analysis was performed by Robertson Microlit Laboratories. Melting points are uncorrected.

(*E*)- and (*Z*)-1-(*p*-Bromophenyl)-2-(2-naphthyl)ethylene (8). A suspension of 2-bromomethylnaphthalene[54] (**6**, 0.44 g, 2.0 mmol) and triphenylphosphine (0.52 g, 2.0 mmol) in 5 mL of dimethylformamide was heated at 150 °C for 30 min. After the solution was cooled to room temperature, *p*-bromobenzaldehyde (0.37 g, 2.0 mmol) and lithium ethoxide (2.2 mL of a 1.0 M solution in ethanol, 2.2 mmol) were added, and the resulting suspension was stirred at room temperature for 3.5 h. The reaction mixture was diluted with 100 mL of diethyl ether and washed successively with 50 mL each of 10% aqueous hydrochloric

(54) Purchased from Aldrich Chemical Co., Milwaukee, WI.

acid, water, and brine. The organic layer was separated and dried over magnesium sulfate, and the solvent was evaporated under reduced pressure. Purification by column chromatography on silica gel with hexane as eluant yielded 0.51 g (82%) of a mixture of cis and trans isomers (cis to trans ratio of ca. 2.5:1 by ^{1}H NMR). For the subsequent photochemical cyclization, the isomers were not separated; however, for characterization purposes, partial separation could be achieved by further column chromatography on silica gel with hexane as eluant.

(*E*)-1-(*p*-Bromophenyl)-2-(2-naphthyl)ethylene (8). Recrystallization from acetone gave colorless plates: mp 188.5−189 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87−7.81 (m, 4 H), 7.73 (dd, J = 8.6 Hz, J = 1.8 Hz, 1 H), 7.52−7.46 (m, 4 H), 7.43 (d, J = 8.8 Hz, 2 H), 7.27 (d, J = 16.4 Hz, 1 H), 7.16 (d, J = 16.4 Hz, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 136.53, 134.65, 133.87, 133.35, 132.04, 129.71, 128.62, 128.25, 128.21, 127.93, 127.08, 126.64, 126.29, 123.58, 121.59; ^{13}C NMR (100 MHz, DMSO-*d*$_6$, δ = 39.51 ppm as internal standard) δ 136.42, 134.44, 133.26, 132.68, 131.68, 129.30, 128.51, 128.28, 127.92, 127.73, 127.64, 126.66, 126.56, 126.18, 123.60, 120.62; UV−vis (hexane) λ$_{max}$ (ε) 230 (23 000), 240 (sh, 13 000), 251 (12 000), 273 (27 000), 282, (30 000), 306 (sh, 31 000), 321 (40 000), 335 (sh, 30 000), 356 (sh, 5900); MS (EI, 70 eV) *m/z* (relative intensity) 310 (46, M+), 308 (45, M+), 229 (64), 228 (100); HRMS, calcd for C$_{18}$H$_{13}$Br (M+) 308.0200, found 308.0201. Anal. Calcd for C$_{18}$H$_{13}$Br: C, 69.92; H, 4.24. Found: C, 69.72; H, 4.19.

(*Z*)-1-(*p*-Bromophenyl)-2-(2-naphthyl)ethylene (8). Recrystallization from methanol gave fine white needles: mp 80−81 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.80−7.77 (m, 1 H), 7.75−7.72 (m, 1 H), 7.72 (s, 1 H), 7.67 (d, J = 8.8 Hz, 1 H), 7.47−7.43 (m, 2 H), 7.35−7.30 (m, 3 H), 7.14 (d, J = 8.0 Hz, 2 H), 6.80 (d, J = 12.4 Hz, 1 H), 6.59 (d, J = 12.0 Hz, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 136.29, 134.62, 133.64, 132.83, 131.58, 131.16, 130.82, 129.46, 128.21, 128.15, 127.90, 127.85, 126.90, 126.35, 126.27, 121.27; UV−vis (hexane) λ$_{max}$ (ε) 229 (44 000), 252 (17 000), 271 (20 000), 302 (17 000); MS (EI, 70 eV) *m/z* (relative intensity) 310 (35, M+), 308 (36, M+), 230 (11), 229 (63), 228 (100); HRMS, calcd for C$_{18}$H$_{13}$Br (M+) 308.0200, found 308.0201. Anal. Calcd for C$_{18}$H$_{13}$Br: C, 69.92; H, 4.24. Found: C, 69.73; H, 4.05.

2-Bromobenzo[*c*]phenanthrene (9). A solution of (*E*)- and (*Z*)-1-(*p*-bromophenyl)-2-(2-naphthyl)ethylene[55] (**8**, 0.50 g, 1.6 mmol), iodine (0.63 g, 2.5 mmol), and propylene oxide[33] (17 mL, 240 mmol) in 1.6 L of benzene was photolyzed in a quartz vessel for 8.5 h in a Rayonet photochemical apparatus equipped with 13 of the 254-nm 35-W mercury lamps. The reaction mixture was then concentrated to 150 mL by rotary evaporation and washed with 15% aqueous sodium thiosulfate, water, and brine. The organic layer was separated and dried over magnesium sulfate, and the solvent was evaporated under reduced pressure. Purification by column chromatography on silica gel with hexane as eluant yielded 0.39 g (78%) of an off-white solid. Recrystallization from methanol gave 2-bromobenzo[*c*]-phenanthrene (**9**) as fine white needles: mp 87−88 °C (lit.[32] mp 86−87.5 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.29 (s, 1 H), 9.05 (d, J = 8.4 Hz, 1 H), 8.04 (d, J = 7.6 Hz, 1 H), 7.93 (d, J = 8.4 Hz, 1 H), 7.90 (d, J = 8.8 Hz, 1 H), 7.87 (d, J = 8.8 Hz, 1 H), 7.85 (d, J = 8.0 Hz, 1 H), 7.83 (d, J = 8.4 Hz, 1 H), 7.75 (t, J = 7.6 Hz, 1 H), 7.72 (d, J = 8.4 Hz, 1 H), 7.66 (t, J = 7.4 Hz, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 133.71, 132.14, 131.74, 131.62, 130.38, 130.25, 129.23, 128.91, 128.37, 127.57, 127.55, 127.21, 126.91, 126.86, 126.53, 126.36, 120.79; ^{13}C NMR (100 MHz, DMSO-*d*$_6$, δ = 39.51 ppm as internal standard) δ 133.15, 131.73, 131.29,

130.85, 130.73, 129.18, 129.14, 129.03, 128.93, 128.39, 127.55, 127.29, 127.19, 126.72, 126.67, 126.46, 125.12, 120.21; UV−vis (hexane) λ$_{max}$ (ε) 218 (39 000), 225 (sh, 35 000), 231 (33 000), 243 (12 000), 253 (sh, 14 000), 264 (sh, 26 000), 274 (52 000), 284 (72 000), 305 (sh, 12 000), 317 (10 000), 329 (sh, 3500); MS (EI, 70 eV) *m/z* (relative intensity) 308 (51, M+), 306 (52, M+), 227 (45), 226 (100); HRMS, calcd for C$_{18}$H$_{11}$Br (M+) 306.0044, found 306.0044. Anal. Calcd for C$_{18}$H$_{11}$Br: C, 70.38; H, 3.61. Found: C, 70.31; H, 3.40.

Flash Vacuum Pyrolysis of 2-Bromobenzo[*c*]phenanthrene. Flash vacuum pyrolyses were performed on 50-mg samples of 2-bromobenzo[*c*]phenanthrene (**9**) at temperatures ranging from 950 to 1100 °C, with a steady flow of nitrogen carrier gas (final pressure: 2.0−2.5 mmHg), as previously described.[56] The crude pyrolysate was purified by flash vacuum chromatography on silica gel with hexane as eluant to yield a mixture of unchanged **9**, benzo[*ghi*]fluoranthene (**4**) and benzo[*c*]-phenanthrene (**14**). The product composition of the mixture varied with the temperature of pyrolysis and was determined by ^{1}H NMR (Table 1). Partial separation of the pyrolysis products **4** and **14** was possible by bulb-to-bulb distillation under reduced pressure. Benzo[*ghi*]fluoranthene (**4**): mp 148−149 °C (lit.[39] 147−149 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.14 (d, J = 6.8 Hz, 2 H), 7.99 (d, J = 8.8 Hz, 2 H), 7.95 (d, J = 8.0 Hz, 2 H), 7.95 (d, J = 8.4 Hz, 2 H), 7.70 (dd, J = 8.0 Hz, J = 6.8 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 137.55, 133.42, 133.25, 128.53, 127.87, 126.90, 126.85, 126.60, 125.25, 123.62; MS (EI, 70 eV) *m/z* (relative intensity) 226 (100, M+).

Flash Vacuum Pyrolysis of 2-Bromobenzo[*c*]phenanthrene-*d*$_4$ (13). Flash vacuum pyrolysis was performed on 50 mg of 2-bromobenzo[*c*]phenanthrene-*d*$_4$ (**13**) at 1050 °C, with a steady flow of nitrogen carrier gas (final pressure: 2.0−2.5 mmHg), as previously described.[56] The crude pyrolysate (32 mg, 86% mass recovery) was purified by flash vacuum chromatography through a short plug of silica with hexane as eluant to yield 28 mg (76%)[57] of a mixture of benzo[*ghi*]fluoranthene-*d*$_4$/*d*$_3$ (**15/16**) and benzo[*c*]phenanthrene-*d*$_4$ (**17/18**) in a ratio of 3:1;[58] no starting material survived. Benzo[*ghi*]fluoranthene-*d*$_4$/*d*$_3$ (**15/16**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.14 (d, J = 6.8 Hz, 1 H), 8.14 (s, small, 1 H), 7.99 (d, J = 8.8 Hz, 1 H), 7.95 (d, J = 8.0 Hz, 1 H), 7.95 (s, 1 H), 7.94 (d, J = 8.8 Hz, 1 H), 7.70 (dd, J = 8.0 Hz, J = 7.2 Hz, 1 H); the presence of **16** was detected by a small singlet at 8.14 ppm. By ^{1}H NMR integration, **15** and **16** formed in a ratio of 2.5:1. Benzo[*c*]-phenanthrene-*d*$_4$ (**17/18**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.15 (d, J = 8.4 Hz, 1 H), 9.15 (s, small, 1H), 8.04 (dd, J = 8.0 Hz, J = 1.6 Hz, 1 H), 7.92 (d, J = 8.4 Hz, 1 H), 7.85 (d, J = 8.4 Hz, 1 H), 7.84 (s, 1 H), 7.70 (td, J = 7.6 Hz, J = 1.6 Hz, 1 H), 7.64 (td, J = 7.4 Hz, J = 1.2 Hz, 1 H); the presence of **17** was detected by a small singlet at 9.15 ppm.

Flash Vacuum Pyrolysis of Benzo[*c*]phenanthrene (14). Flash vacuum pyrolysis was performed on 50 mg of benzo[*c*]phenanthrene at 1050 °C, with a steady flow of nitrogen carrier gas (final pressure: 2.0−2.5 mmHg), as previously described.[56] The crude pyrolysate (47 mg, 94% mass recovery) was purified by preparative thin-layer chromatography on silica gel with hexane as eluant to yield 28 mg (56%) of a mixture of benzo[*ghi*]fluoranthene (**4**, 12%), cyclopenta-[*cd*]pyrene (**19**, 10%)[51] and unchanged benzo[*c*]phenanthrene (78%).[58]

Supporting Information Available: Experimental procedures for the syntheses of [1,3,4,5-^{2}H$_4$]-2-bromobenzo[*c*]-phenanthrene (**13**) and benzo[*c*]phenanthrene (**14**). NMR spectra of the synthetic intermediates, pyrolysis precursors, and pyrolysis products (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(55) The ultraviolet light that causes photocyclization also interconverts the (*E*)- and (*Z*)-stilbene isomers; therefore, either isomer (or a mixture of isomers) can be used for the photochemical ring closure.

(56) For a more detailed description of the apparatus and the procedure, see: Scott, L. T.; Bratcher, M. S.; Hagen, S. *J. Am. Chem. Soc.* **1996**, *118*, 8743−8744.

(57) Yield of purified mixture (%) after separation from higher molecular weight byproducts by flash vacuum chromatography.

(58) Determined by integration of the ^{1}H NMR spectra of the purified mixture of monomeric products.