

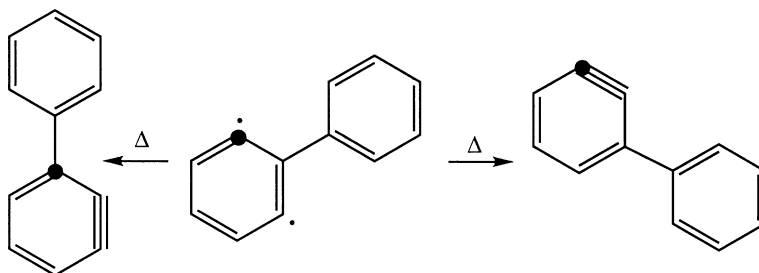
Article

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J. Am. Chem. Soc., **2003**, 125 (21), 6485-6490 • DOI: 10.1021/ja0213672 • Publication Date (Web): 01 May 2003

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A *m*-Benzyne to *o*-Benzyne Conversion through a 1,2-Shift of a Phenyl Group

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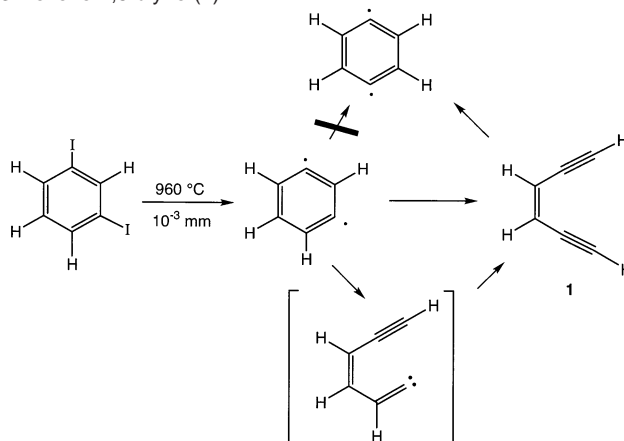
Abstract: Pyrolysis of two differently labeled versions of 3-phenylphthalic anhydride shows that a *m*-benzyne can form the related *o*-benzyne through shift of a phenyl group. The highest energy point in the process is the transition structure for a reverse carbon–hydrogen insertion in an intermediate benzopentalene. With the minor addition of an intermediate alkyne formed through a Roger Brown rearrangement, the original mechanism for formation of acenaphthalene accommodates the labeling results.

Introduction

Almost 40 years ago, Fisher and Lossing suggested that one benzyne might be forming another, when they found 3-hexen-1,5-diyne (**1**), a product characteristic of *p*-benzyne, upon pyrolysis of 1,3-diiodobenzene.¹ As the authors made clear, however, this observation does not necessarily require a 1,2-hydrogen shift converting *m*-benzyne into *p*-benzyne. For example, stepwise processes, in which only one iodine is initially lost, could produce either *p*-benzyne or **1** without the intermediacy of *m*-benzyne. A more likely mechanism for the conversion of *m*- to *p*-benzyne is either an initial ring-opening to yield a transient vinylidene followed by rapid rearrangement to **1** or a concerted ring-opening and hydrogen migration, directly transforming *m*-benzyne into **1** (Scheme 1),^{2,3} and thence to *p*-benzyne. Convincing experimental evidence has yet to be found that suggests that *o*-benzyne can isomerize into either *m*- or *p*-benzyne, or vice versa.⁴

The heats of formation at 298 K (ΔH_f° , 298) for *o*-, *m*-, and *p*-benzyne are 106 ± 3 , 122 ± 3 , and 138 ± 3 kcal/mol, respectively,⁵ indicating that a cascade from *p*- to *o*-benzyne would be relentlessly exothermic. Of course, the high barrier for similar 1,2-hydrogen shifts in simple alkyl⁶ and aryl⁷ radicals is likely to be present substantially in the benzyne systems as well and may kinetically prevent these isomerizations. However, if the

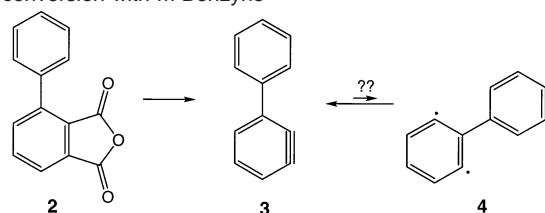
Scheme 1. Pyrolytic Conversion of 1,3-Diiodobenzene to 3-Hexene-1,5-diyne (**1**)



adjacent hydrogen atom were changed to a substituent that could migrate more easily, these isomerizations may be observable.⁸ We chose to study the rearrangements of phenyl-substituted

- (1) Fisher, I. P.; Lossing, F. P. *J. Am. Chem. Soc.* **1963**, *85*, 1019.
 (2) (a) Sander, W. *Acc. Chem. Res.* **1999**, *32*, 669. (b) 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.
 (3) (a) The reaction energies and barriers for the direct 1,2-hydrogen shifting processes constituting the *p*- to *m*- to *o*-benzyne cascade have been calculated for parent benzyne at the RCCSD(T)/6-31G(d,p)//B3LYP/6-31G(d) and G2M/B3LYP/6-31G(d) levels of theory.^{3b} The computed barrier for formation of *o*-benzyne from *m*-benzyne (56.3 kcal/mol) is 4.4 kcal/mol lower than the barrier for formation of *p*-benzyne (60.7 kcal/mol). This result would predict that pyrolysis of *m*-benzyne would predominantly yield products from *o*-benzyne, rather than from *p*-benzyne. In addition, neither stepwise nor concerted ring-opening and hydrogen migration processes, as shown in Scheme 1, were considered. The concerted H-migration and ring-opening process converting *m*-benzyne into 3-hexen-1,5-diyne is predicted to have a barrier of approximately 50 kcal/mol at the B3LYP/6-31G(d,p) level.^{2a} (b) Moskaleva, L. V.; Madden, L. K.; Lin, M. C. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3967.

- (4) (a) The isomerization of one *o*-benzyne into another *o*-benzyne via an apparent hydrogen migration has been observed in the pyrolytic generation of 1,6-¹³C-*o*-benzyne as a minor pathway.^{4b} Whether or not this proceeds via another benzyne isomer, or even whether it is intramolecular, is a matter of speculation. It is quite possible that, at the highest temperatures studied (830 °C), the participation of *m*- and/or *p*-benzyne is simply not observable. Several papers have approached this question both theoretically and experimentally,^{4c} and there is some evidence for the interconversion of the parent benzyne over or through very high barriers. Changing the migrating group to phenyl introduces the possibility of a mechanism in which the π system of the phenyl interacts with the σ orbital of the benzyne, thus making the rearrangement process easier. As a referee has quite correctly implied, the price of this increased ease of investigation is lack of relevance to the parent system, which we are explicitly not considering here. (b) Barry, M.; Brown, R. F. C.; Eastwood, F. W.; Gunawardana, D. A.; Vogel, C. *Aust. J. Chem.* **1984**, *37*, 1643. (c) Diau, E. W.-G.; Casanova, J.; Roberts, J. D.; Zewail, A. H. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 1376. Wang, H.; Laskin, A.; Moriarty, N. W.; Frenklach, M. *Proc. Combust. Inst.* **2000**, *28*, 1545. Moskaleva, L. V.; Madden, L. K.; Lin, M. C. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3967.
 (5) Wenthold, P. G.; Squires, R. R.; Lineberger, W. C. *J. Am. Chem. Soc.* **1998**, *120*, 5279.
 (6) Wilt, J. W. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Chapter 8.
 (7) Brooks, M. A.; Scott, L. T. *J. Am. Chem. Soc.* **1999**, *121*, 5444.

Scheme 2. Formation of *o*-benzyne and Its Potential Interconversion with *m*-Benzyne

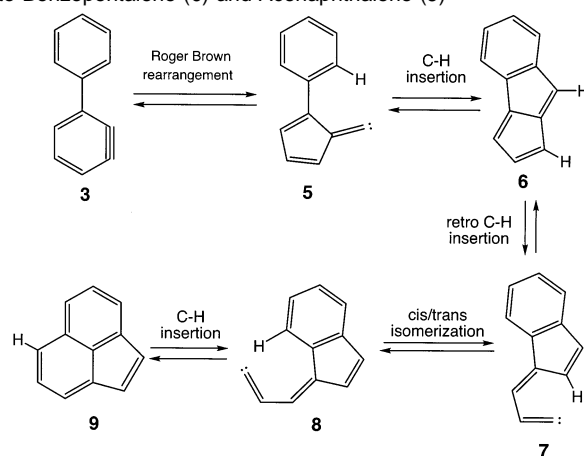
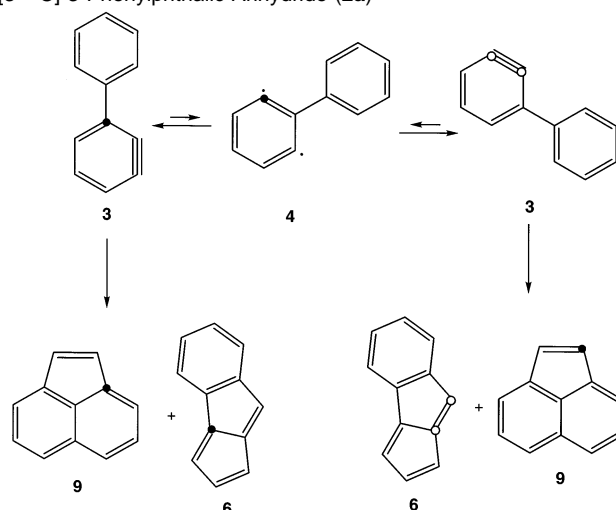
o-benzyne⁹ (**3**), made through pyrolysis of 3-phenylphthalic anhydride (**2**) (Scheme 2). The phenyl substituent can be reasonably expected¹⁰ to undergo more facile migration than hydrogen.¹¹ Indeed, 1,2-migrations of phenyl groups to radicals are known in aromatic systems.^{12,13} However, by entering the potential equilibration from the *o*-benzyne side, we do take the risk that the lower energy *o*-benzyne will not be able to climb the energetic hill to the higher energy *m*-benzyne before passing on to its ultimate fate.

Results and Discussion

The flash vacuum pyrolysis of **2** has been used previously¹⁴ to study the thermal chemistry of **3**, which yields cyclopent[*a*]-indene (benzopentalene, **6**) as the primary rearrangement product, with acenaphthalene (**9**) being formed by a subsequent rearrangement of **6**. The generally accepted mechanism is shown in Scheme 3.¹⁵

To observe phenyl migration in **3**, a label must be placed that would be scrambled by the isomerization of *o*- to *m*-benzyne and back.¹⁶ Our initial experiment involved ¹³C-labeling the *ipso* carbon in **3**, which would scramble via *o*- to *m*-benzyne isomerization, to give labeled **6** and **9** as shown in Scheme 4.

In the products formed following *o*- to *m*-benzyne interconversion, the label ends up as one of the two triply bonded

Scheme 3. Mechanism for Conversion of 3-Phenyl-*o*-benzyne (**3**) into Benzopentalene (**6**) and Acenaphthalene (**9**)**Scheme 4.** Predicted Labeled Products from Pyrolysis of [¹³C]-3-Phenylphthalic Anhydride (**2a**)

- = 100% label abundance
- = 50% label abundance - The label is scrambled through vinylidene **5** (Scheme 3)

carbons in the resultant *o*-benzyne, which are equilibrated via 2-phenylcyclopentadienylidene carbene.^{17,18} Thus, in the primary rearrangement product, **6**, there are two positions that should each have 50% of the label. In the secondary product, **9**, an additional symmetry element is gained, as the two positions become equivalent, and the 1-position of **9** is predicted to receive 100% of the label.

It has been suggested¹⁸ that the scrambling of the two triply bonded carbons in *o*-benzyne is not the result of equilibration via cyclopentadienylidene carbene, but occurs through a stepwise decomposition of the anhydride. Fortunately, it matters not for this experiment whether the benzyne or cyclopentadienylidene carbene is formed initially, as there is no simple mechanism that accomplishes the label scrambling shown in Scheme 4 directly from the cyclopentadienylidene carbene. It is certainly possible to construct alternative schemes that do generate **4** from **2** in a stepwise manner without the intermediacy of **3**. However, the reformation of **3** from **4** is not subject to

- (8) In fact, the migration of a TMS group in a *p*-benzyne to form a *m*-benzyne has been suggested in the high-temperature pyrolysis of a TMS-substituted enediyne: Johnson, G. C.; Stofko, J. J., Jr.; Lockhardt, T. P.; Brown, D. W.; Bergman, R. G. *J. Org. Chem.* **1979**, *44*, 4215.
- (9) (a) It may seem more sensible to generate **4**, rather than **3**, because the desired phenyl shift would then be exothermic. Unfortunately, it can always be argued that stepwise decomposition of any potential precursor to **4** could conceivably bypass **4** and still give **3**. Accordingly, we started instead with labeled **3** and hoped that the endothermic isomerization to **4** would compete with the formation of the ultimate products. (b) In ref 2b, Brown et al. formed **4** by pyrolysis (1000–1100 °C) of diallyl biphenyl-2,6-dicarboxylate and observed only a small yield of products nominally deriving from 3-phenyl-*o*-benzyne. Approximately 85% of the products were unidentified aromatic compounds.^{2b}
- (10) Wilt, J. W. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; p 346 ff.
- (11) We completely ignore the question of whether the phenyl migration occurs in one or two steps.
- (12) Preda, D. V.; Scott, L. T. *Org. Lett.* **2000**, *2*, 1489.
- (13) Preda, D. V.; Scott, L. T. *Polycyclic Aromat. Compd.* **2000**, *19*, 119.
- (14) (a) Reference 2b. (b) Brown, R. F. C.; Choi, N.; Eastwood, F. W. *Aust. J. Chem.* **1995**, *48*, 185. (c) Brown, R. F. C.; Choi, N.; Coulston, K. J.; Eastwood, F. W.; Wiersum, U. E.; Jennekens, L. W. *Tetrahedron Lett.* **1994**, *35*, 4405.
- (15) Scheme 3 is essentially the mechanism given¹⁴ by Brown, with one addition and one omission. The cis/trans isomerization step is not present (although obviously implied) in refs 2b, 14b, or 14c. It is included here in Scheme 3 for clarity. Also, in refs 2b and 14b, an additional possible pathway between **6** and **9** is presented, single bond scission in **6** to yield a diradical. This step is not included in Scheme 3, as it seems highly unlikely that the required diradical intermediate could compete energetically with the vinylidene, especially given the well-known rearrangement between vinylidenes and terminal acetylenes.
- (16) In ref 2b, Bapat, et al. also studied the FVP (1020 °C) of [2,3-¹³C₂]-3-phenylphthalic anhydride and did not report any products of phenyl migration in the doubly labeled *o*-benzyne intermediate **3**. It is possible that phenyl migration did not occur in **3** under their conditions or that the doubly labeled products resulting from a small amount of scrambled **3** were overlooked. Their pyrolyses were performed on samples that were diluted with unlabeled **2**, such that only 10% was doubly labeled.^{2b}

- (17) (a) See ref 4b. (b) Brown, R. F. C.; Coulston, K. J.; Eastwood, F. W.; Vogel, C. *Aust. J. Chem.* **1988**, *41*, 1687.
- (18) Wentrup, C.; Blanch, R.; Briehl, H.; Gross, G. *J. Am. Chem. Soc.* **1988**, *110*, 1874.

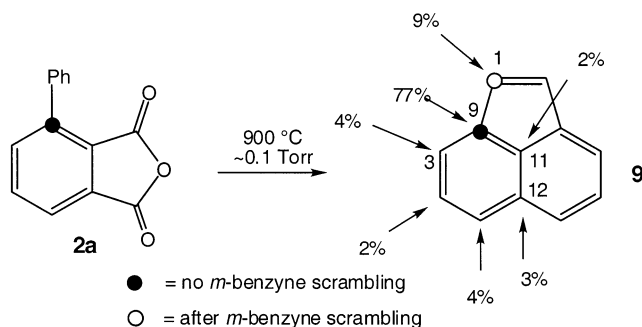
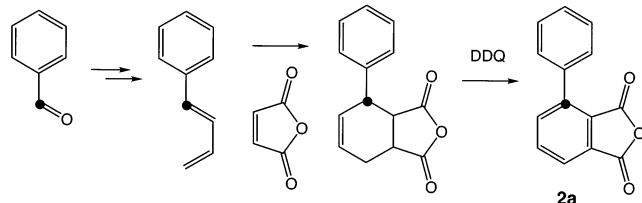


Figure 1. Isotopic enrichment over natural abundance in ¹³C-labeled **6**, produced by pyrolysis of **2a** at 900 °C and ~0.1 Torr.

Scheme 5. Synthesis of [3-¹³C]-3-Phenylphthalic Anhydride (**2a**)



these concerns. However we get to **4**, the return to **3** must involve a benzyne-to-benzyne rearrangement.

The necessary labeled precursor, [3-¹³C]-3-phenylphthalic anhydride (**2a**), was synthesized (Scheme 5) following the method of Sissman¹⁹ as elaborated by Brown.^{14b} A label was introduced at the *ipso* position by starting with labeled benzaldehyde, which was itself made from commercially available labeled benzoic acid.

In the analysis of our pyrolysate, we chose to examine only the labeled acenaphthalene, **9**. Under our conditions, the major product,¹⁴ **6**, was not isolated; rather, it dimerized quickly when brought to room temperature.^{14c} Given that three possible isotopomers of **6** are predicted in Scheme 4, there are six possible isotopomers of the dimer. In accordance with this prediction, we found the ¹³C spectrum of the labeled benzopentalene dimer to be too complex to be evaluated. No attempts were made to perform low-temperature NMR spectroscopy on **6** itself, or to trap **6** to give an analytical sample,^{14c} because, in theory, all necessary information can be derived from the ¹³C spectrum of labeled **9**.

When **2a** was sublimed through a quartz tube at 900 °C and ~0.1 Torr, the isolated acenaphthalene was ¹³C-enriched as shown in Figure 1.

As can be seen in Figure 1, most of the label appears at the 9 position, exactly where the conventional mechanism would place it. Yet there is significant enrichment at position 1, indicating the some symmetrization has occurred, most likely through *m*-benzyne **4**, as shown in Scheme 4. The baseline enrichment of positions that “cannot” receive a ¹³C label seems to be about 2–3%.²⁰ In addition, at temperatures ≥900 °C, significant label “leaks” to other positions, exactly as predicted by the Scott “6–5” benzenoid ring-contraction–ring-expansion mechanism.²¹ In this process, the skin of acenaphthalene rotates about the central quaternary carbon 11 four positions clockwise or counterclockwise. At 900 °C, the Scott rearrangement appears to be transferring approximately 1% of the label at position 9

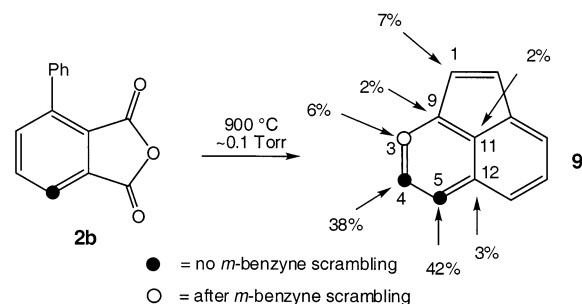
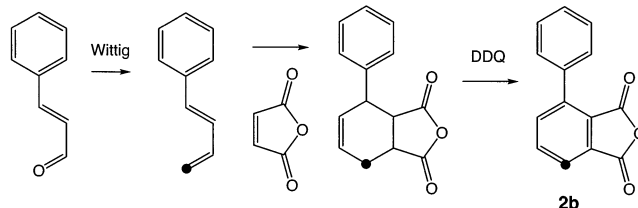


Figure 2. Isotopic enrichment over natural abundance in ¹³C-labeled **6**, produced by pyrolysis of **2b** at 900 °C and ~0.1 Torr.

Scheme 6. Synthesis of [6-¹³C]-3-Phenylphthalic Anhydride (**2b**)



to positions 3 and 12.²² Although the first wave of Scott rearrangements cannot populate position 1, such a transfer will become important in future discussions of other labeling experiments. Accordingly, we see position 1 as having 6–7% excess label, which means that 12–14% of the reaction involved symmetrization through *m*-benzyne **4**.

A second labeling experiment was subsequently performed, in which the “para” position in the anhydride precursor was ¹³C-labeled (**2b**). The synthesis of **2b** was accomplished by a simple Wittig reaction on cinnamaldehyde (Scheme 6).

The standard mechanism predicts that the label should appear in the 5 position without scrambling and, if scrambling via *m*-benzyne **4** occurs, in the 3 position as well (Scheme 3). Pyrolysis of **2b** at 900 °C and ~0.1 Torr yielded acenaphthalene in which the excess label was distributed as shown in Figure 2.

The isotopic enrichments shown in Figure 2 clearly show that Scheme 3 does not account for all chemical processes occurring in the pyrolysis. The scrambling of positions 4 and 5 in **9** is not predicted by the mechanism given in Scheme 3. Fortunately, there is a simple addition to the mechanistic picture that accounts for the observed scrambling. It has been shown that under pyrolytic conditions, 1-phenyl-1-buten-3-yne undergoes scrambling of the acetylenic carbons via a vinylidene by a process consisting of both a hydrogen migration and a styryl migration.²³ This process is analogous to the acetylenic scrambling observed in ¹³C-labeled phenylacetylene, the Roger Brown rearrangement.²⁴ Thus, **7** and **8**, the two vinylidenes shown in Scheme 3, can reversibly form the corresponding alkyne by

(20) Position 11 of **9** (the central carbon) should not receive any ¹³C-enrichment, either by the scrambling shown in Scheme 4 or by the ratcheting mechanism in **9**.²¹ The reported enrichment percentages are based on the ¹³C NMR spectrum acquired with a 120 s delay, in which the longest ¹³C T₁ in **9** was estimated to be approximately 12 s. The overestimation of ¹³C-label in positions that should not receive any enrichment is likely the result of errors in comparing the relative integrations.

(21) Scott, L. T.; Roelofs, N. H. *Tetrahedron Lett.* **1988**, 28, 6857.

(22) Professor Scott has kindly informed us that pyrolysis of **2a**-¹³C-labeled acenaphthalene above 900 °C reveals exactly that: specific leakage of the label to positions 3 and 12 in the first generation product. Racoveanu, A.; Scott, L. T., personal communication with permission to cite.

(23) Schulz, K.; Hofmann, J.; Zimmermann, G.; Findeisen, M. *Tetrahedron Lett.* **1995**, 36, 3829.

(24) Brown, R. F. C.; Eastwood, F. W.; Harrington, K. J.; McMullen, G. L. *Aust. J. Chem.* **1974**, 27, 2393.

(19) Sissman, E. E.; Murray, R. J.; McChesney, J. D.; Houston, L. L.; Pazdemik, T. L. *J. Med. Chem.* **1976**, 19, 148.

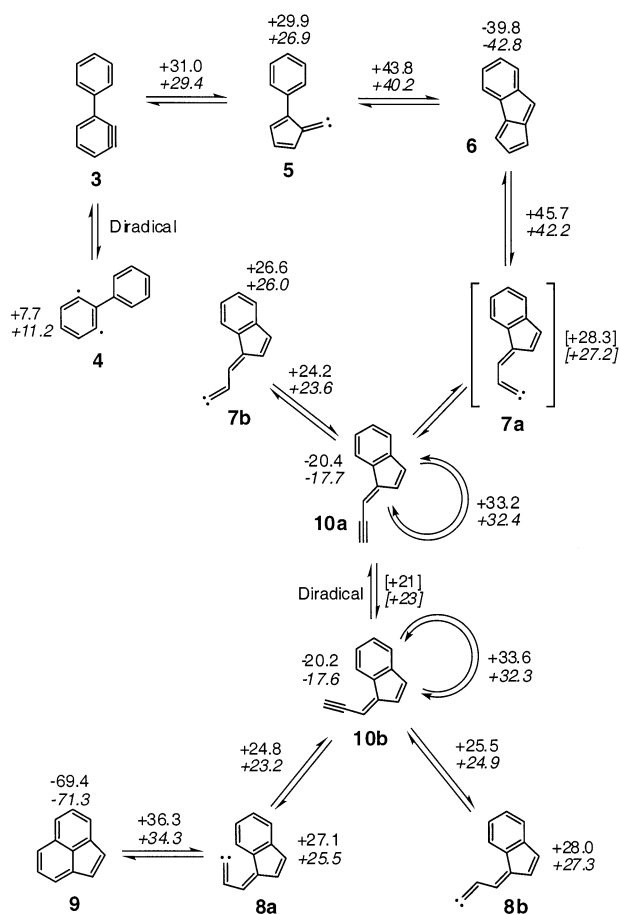


Figure 3. Computed enthalpies at 900 °C, relative to 3-phenyl-*o*-benzynes (3), in kcal/mol. Nonitalicized numbers are at B3LYP/6-311+G**^a; italicized numbers are at CCSD(T)/cc-pVDZ.

either H-migration or vinyl migration prior to formation of acenaphthalene by C–H insertion. In addition, this terminal acetylene scrambling could occur either before or after the *cis*/*trans* isomerization of the exocyclic alkene. It is this process that accounts for the nearly perfect scrambling of the label between positions 4 and 5 in the pyrolysis of **2b**.

Position 3 shows a slight enrichment of 6%, 3–4% above the baseline, which corresponds to 6–8% scrambling through *m*-benzynes. Interestingly, position 1 also shows nonnegligible enrichment. Although it is fed by Scott rearrangement from both positions 4 and 5,^{21,22} that process should only account for an additional 1–2%, based on the first labeling experiment. Thus, we cannot fully account for the amount of label observed in position 1.

In addition to the labeling studies detailed above, we analyzed the proposed mechanistic pathway computationally. All geometries were optimized at the B3LYP/6-311+G** level of theory, and the electronic energies were refined by performing CCSD(T)/cc-pVDZ single point calculations for each stationary point. The computational results are summarized in Figure 3.

Several points are worth mentioning. First, because of the size of the system, believable enthalpies were not available for the two processes that require significantly diradicaloid transition structures or intermediates – the *o*- to *m*-benzynes isomerization (**3** to **4**) and the *cis*/*trans* isomerization of ethynylbenzofulvene (**10**).²⁵ The restricted density functional theory (DFT) method B3LYP we employed for our geometry optimizations fails for

true diradicals, and a multireference method would require a (16/16) active space for the benzyne isomerization and a (14/14) active space for the *cis*/*trans* isomerization, putting the computational cost too high. In addition, the benzyne isomerization does not lend itself to approximation by model compound investigation. Thus, although a computational value for the activation enthalpy for the phenylbenzyne isomerization is obviously of great interest, we are unable (at present) to provide one. For the ethynylbenzofulvene isomerization (**10a** to **10b**), an approximate enthalpic barrier of ~41 kcal/mol was obtained from multireference calculations on a model compound, which gives the bracketed numbers shown for that process in Figure 3.²⁶ Second, although the equilibrium between terminal alkynes and vinylidenes has become very commonly invoked in explaining the pyrolytic chemistry of alkynes,^{23,24,27} it appears that, at least at the level of theory employed here, the vinylidene structures (**7** and **8**) produced from migration of the hydrogen in ethynylbenzofulvenes **10a** and **10b** are not even minima. For **7b**, **8a**, and **8b**, B3LYP/6-311+G** optimizations resulted in energetic minima which, upon inclusion of zero-point energy and integrated heat capacity, were higher in enthalpy than their corresponding transition structures for formation of **10a** or **10b**.²⁸ Vinylidene **7a** was not even found to be an energetic minimum. Rather, the energy given in Figure 3 for **7a** corresponds to the relative electronic energy of an inflection point where the slope of energy versus atomic displacement is, while still negative, closest to zero.²⁹ That is, the C–H insertion reactions that produce benzopentalene (**6**) and acenaphthalene (**9**), from *trans*-(**10a**) and *cis*-ethynylbenzofulvene (**10b**), respectively, each proceed over a single transition structure through species that are electronically vinylidenes, but which are not energy minima. Attempts were made to identify the energetic minima on either side of the transition state, but IRC calculations failed. That no local minimum exists for these vinylidene “intermediates” has been noticed before by Cioslowski et al.³⁰

- (25) (a) Both the *o*- and the *m*-benzynes have some diradical character, and RB3LYP will almost certainly overestimate the zwitterionic nature of the wave function, resulting in predictable geometric deviations and less predictable energetic fluctuations.^{25b} This failure is a quantitative, as opposed to the qualitative, failure of restricted DFT to compute the wave functions of pure diradicals, such as the transition structures and/or intermediates involved in the *o*- to *m*-phenylbenzynes isomerization and the terminal alkyne π -bond rotation. The performance of DFT for the vinylidene structures should be much better, as they are well described by a single configuration.^{25c} Regardless of the failures of DFT to give reliable energetics, the energies should be improved by the use of CCSD(T). (b) Cramer, C. J.; Nash, J. J.; Squires, R. R. *Chem. Phys. Lett.* **1997**, 277, 311. (c) Chen, W.-C.; Yu, C.-h. *Chem. Phys. Lett.* **1997**, 277, 245.
- (26) The model compound used to approximate the terminal alkyne isomerization was ethynylfulvene. Two 1-*A'* C_v geometries were optimized at the (10/10)CASSCF/6-311+G** level of theory: one with the alkyne in the plane of the molecule, and one with the alkyne rotated 90°. Vibrational analysis showed the planar geometry to be a minimum and the rotated geometry to be a transition state (exactly one mode with an imaginary frequency). The electronic energies were refined by performing (10/10)CASPT2/6-311+G** single point calculations at the CASSCF optimized geometries. The CASSCF zero-point energies and integrated heat capacities were added to the CASPT2 energies to give a value of $\Delta H^\ddagger = 40.8$ kcal/mol for rotation about the fulvene double bond in ethynylfulvene.
- (27) See, and references therein: (a) Brown, R. F. C. *Eur. J. Org. Chem.* **1999**, 3211. (b) Brown, R. F. C. *Recl. Trav. Chim. Pays-Bas* **1988**, 107, 655.
- (28) The electronic energy minima for these vinylidenes are extremely shallow: 0.2 kcal/mol for **7b**, 0.2 kcal/mol for **8a**, and 0.1 kcal/mol for **8b**, all at the B3LYP/6-311+G** level of theory. The CCSD(T)/cc-pVDZ relative electronic energies for these B3LYP saddle point geometries are very similar: 0.3 kcal/mol for **7b**, 0.2 kcal/mol for **8a**, and 0.1 kcal/mol for **8b**.
- (29) This inflection point was obtained by performing a relaxed scan of the C–H angle involving the two vinylidene carbons and the migrating hydrogen atom, with 1° increments. At the approximate inflection point, the C–C–H angle was 91.6°, and the electronic energy (B3LYP/6-311+G**) was –462.042301 hartrees. The slope at this point was approximately –0.005 kcal/mol per degree.

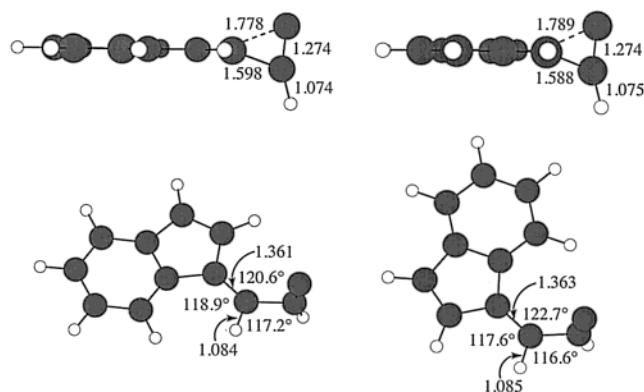
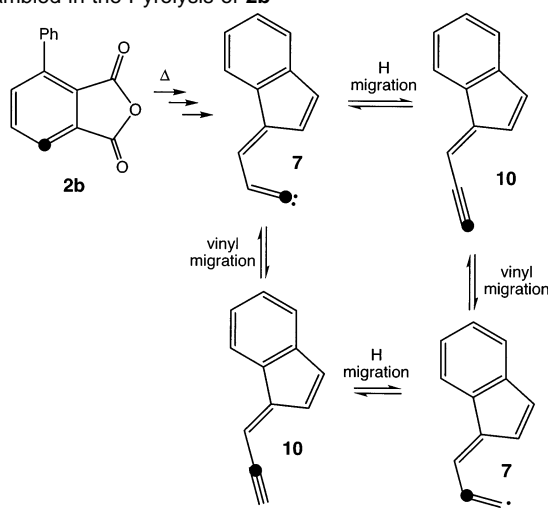


Figure 4. Two views of the transition structures for scrambling the two acetylenic carbons in **10a** (left) and **10b** (right). Geometries were optimized at B3LYP/6-311+G**. Bond lengths are in Ångstroms, and angles are in degrees.

Scheme 7. Mechanism by Which the Acetylenic Positions Are Scrambled in the Pyrolysis of **2b**



In addition to the C–H insertion reactions, the process by which the two acetylenic carbons in **10a** and **10b** are equilibrated (indicated by the curved arrows in Figure 3) was also found to occur through a single transition structure, rather than the two-step process shown in Scheme 7 and postulated in refs 23 and 24. The transition structures for the scrambling processes in **10a** and **10b** are shown in Figure 4.

The structures shown in Figure 4 clearly show that the “styryl” migration (in this case, a “benzofulvenyl” migration) is a nonplanar process in which the migrating sp^2 carbon orients its p orbital along the long axis of the alkyne, allowing a favorable interaction between the exocyclic fulvene π -bond and one of the π^* molecular orbitals in the alkyne. This interaction is also evident in the length of the triple bond, which at 1.274 Å is considerably longer than those in **10a** and **10b** (1.207 and 1.208 Å).³¹ These transition structures could be considered “late” in that the terminal carbon of the alkyne is closer to the sp^2 migrating carbon (1.598 and 1.588 Å) than is the internal carbon (1.778 and 1.789 Å). That is, the benzofulvenyl migration is more than half complete. Yet when it is considered that there is no energetic minimum prior to the scrambled ethynylben-

zofulvene, and that the required hydrogen atom migration has virtually not even begun in the transition structures, they could also be viewed as fairly “early” transition structures.

It is always possible, of course, that systematic error inherent in the optimization method is resulting in artifactual behavior and that the vinylidenes are, in fact, minima. Lineberger and co-workers found a 3.4 kcal/mol classical barrier for hydrogen migration in vinylvinylidene, employing CISD/D95(d,p).³² They also estimated the lifetime of singlet vinylvinylidene to be 20–200 fs by analysis of the photoelectron spectrum of its negative ion.^{32a} On the other hand, Schaefer and co-workers found that, at the highest level investigated (CCSD(T)/TZ2P//CCSD/TZ2P), ethynylvinylidene has a vanishingly small classical barrier for formation of diacetylene.³³ A fairly systematic comparison of several DFT methods^{25c} with the estimated coupled-cluster complete basis set limiting value³⁴ found that, at B3LYP/aug-cc-pVTZ, the classical barrier height for the isomerization of parent vinylidene to acetylene was overestimated by 1.0 kcal/mol (with B3LYP/aug-cc-pVTZ, the barrier was 3.9 kcal/mol, whereas the coupled-cluster CBS limit was 2.9 kcal/mol).³⁵ Therefore, the method error associated with B3LYP apparently works to raise the barrier associated with hydrogen migration in vinylidenes rather than lower it, and the finding that the vinylidenes in Figure 3 are not minima is probably not artifactual. As mentioned earlier, this observation is not new.³⁰

Comparison of the computed potential energy surface with the experimental results shows an overall qualitative agreement. The retro C–H insertion from benzopentalene (**6**) to form *trans*-ethynylbenzofulvene (**10a**) is computed to be the highest point along the reaction path by about 2 kcal/mol. This result is consistent with the observation that benzopentalene is the major product of the pyrolysis.¹⁴ The final C–H insertion step to form acenaphthalene (**9**) is computed to be slightly higher than the barriers for carbon scrambling in ethynylbenzofulvene (**10**): about 2 kcal/mol with CCSD(T) and 3 kcal/mol with B3LYP. This calculation is in qualitative agreement with the observation that positions 4 and 5 are scrambled in the acenaphthalene product (see Figure 2).³⁶ Although we were unable to calculate the barrier for phenyl migration in *o*-benzynes, the observation of 6–14% scrambling through *m*-benzynes indicates that the barrier is slightly higher than that for the benzopentalene retro

(31) This lengthening is also more significant than in the transition structure connecting vinylidene with acetylene. At the B3LYP/6-311+G** level of theory, the C–C distance in the transition structure is 1.250 Å, whereas it is 1.199 Å in acetylene. Thus, the triple bond is lengthened by 0.051 Å in the transition structure connecting vinylidene and acetylene, but by 0.067 Å in the transition structure for acetylenic carbon scrambling in *trans*-ethynylbenzofulvene, **10a**.

(32) (a) Gunion, R. F.; Köppel, H.; Leach, G. W.; Lineberger, W. C. *J. Chem. Phys.* **1995**, *103*, 1250. (b) The CISD/D95(d,p) calculations reported in ref 28a gave a nonplanar transition structure for hydrogen migration in vinylvinylidene. They report that a planar transition structure optimization resulted in a second-order saddle point. We observed no such tendency toward nonplanarity in the hydrogen migration transition structure, in that all three transition structures we found for hydrogen migration reactions were planar and had exactly one mode with an imaginary frequency. (c) In ref 33, Schaefer and co-workers calculated classical barriers of 2.7 kcal/mol at CISD/DZP and 2.6 kcal/mol at CISD/TZ2P for hydrogen migration in ethynylvinylidene, but 0.05 kcal/mol at CCSD(T)/TZ2P//CCSD/TZ2P. It is possible that the barrier for hydrogen migration in vinylvinylidene obtained by CISD/D95(d,p)^{32a} would drop when higher correlated methods and/or larger basis sets were used.

(33) Collins, C. L.; Hu, C.-H.; Yamaguchi, Y.; Schaefer, H. F., III. *Isr. J. Chem.* **1993**, *33*, 317.

(34) Chang, N.-Y.; Shen, M.-Y.; Yu, C.-h. *J. Chem. Phys.* **1997**, *106*, 3237.

(35) When using the 6-311+G** basis set, we found that the overestimation by B3LYP is even larger. The classical barrier for the hydrogen migration in vinylidene was computed to be 4.4 kcal/mol at B3LYP/6-311+G**, 1.5 kcal/mol larger than the coupled cluster CBS limit.

(30) Cioslowski, J.; Schimeczek, M.; Piskorz, P.; Moncrieff, D. *J. Am. Chem. Soc.* **1999**, *121*, 3773. We thank Professor L. T. Scott for alerting us to this reference. Sander, W.; Exner, M.; Winkler, M.; Balster, A.; Hjerpe, A.; Kraka, E.; Cremer, D. *J. Am. Chem. Soc.* **2002**, *124*, 13072.

C–H insertion step. Manipulation of the Eyring equation³⁷ gives a value of $\Delta\Delta G_{1173}^\ddagger = 6.4$ kcal/mol for 6% scrambling and 4.2 kcal/mol for 14%. Therefore, we can provide an estimate of 46–52 kcal/mol for the barrier to phenyl migration in *o*-benzyne.

Conclusion

The labeling results described in these two sets of experiments show that *m*-benzene **4** is able to form *o*-benzyne **3** through shift of a phenyl group. Although they are highly suggestive, they do not absolutely demand that **3** be able to form **4** through a phenyl shift. They also reveal the need to elaborate slightly Roger Brown's original mechanism for the formation of acenaphthalene from 3-phenylphthalic anhydride to include, ironically, an alkyne formed through a Roger Brown rearrangement.

Experimental Section

General. NMR spectra were recorded on Varian Mercury 300, Varian-Unity INOVA 400, and Varian-Unity INOVA 500 NMR spectrometers. Chemical shifts are reported in parts per million (ppm, δ) and were indirectly referenced to TMS (tetramethylsilane) by employing known solvent resonances as internal standards. Coupling constants (*J*) are reported in Hertz (Hz).

Computational Methodology. All geometry optimizations and vibrational analyses were performed using the B3LYP³⁸ density functional method and the standard Pople basis set 6-311+G**. All structures (except for **7a**) were shown to be electronic minima (no vibrational modes with imaginary frequencies) or transition structures (exactly one vibrational mode with an imaginary frequency). The energies of the B3LYP optimized geometries were refined by performing CCSD(T)³⁹ single-point calculations, using Dunning's cc-pVDZ basis set.⁴⁰ The zero-point and thermal corrections from the B3LYP vibrational analyses were used without scaling to convert the B3LYP and CCSD(T) electronic energies to enthalpies at 1173 K. All of the calculations were carried out with the Gaussian 98 package of electronic structure programs.⁴¹

- (36) The $\Delta\Delta H^\ddagger = 2-3$ kcal/mol difference between scrambling and acenaphthalene formation would not actually account for the extent of scrambling at 900 °C, which is roughly 95%. Manipulation of the Eyring equation gives $k_1/k_2 = \exp(\Delta\Delta G^\ddagger/RT)$. 95% scrambling corresponds to a relative rate of 19:1, so at 1173 K, $\Delta\Delta G^\ddagger = 6.9$ kcal/mol. An error of 1–2% in the NMR integrations could stretch this to a relative rate of 10:1, but that still comes to $\Delta\Delta G^\ddagger = 5.4$ kcal/mol. Thus, while the computational results agree qualitatively, there is a slight quantitative disagreement. Of course, the reported relative enthalpies at 900 °C neglect a sizable contribution from entropy. When the relative Gibbs free energies at 900 °C are compared, the $\Delta\Delta G_{1173}^\ddagger = 4.9$ and 5.6 kcal/mol with B3LYP, and $\Delta\Delta G_{1173}^\ddagger = 4.4$ and 4.1 kcal/mol with CCSD(T). In addition, a statistical effect favors scrambling, because it can occur from either of the two isomers of **10**.
- (37) For scrambling of 6–14%, the relative reaction rates are 15.7:1 and 6.1:1, and thus $\Delta\Delta G_{1173}^\ddagger = 6.4$ and 4.2 kcal/mol, respectively.³⁶
- (38) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.
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Flash Vacuum Pyrolysis of Anhydrides **2a and **2b**.**¹⁴ Typically, 50 mg of anhydride (**2a** or **2b**) was sublimed into a hot quartz tube (750–1100 °C) under reduced pressure (~100 mTorr). The pyrolysate was condensed on a dry-ice-cooled surface. The receiving vessel was washed with CH₂Cl₂ (10 mL), and the solvent was removed. The reaction mixture was purified by flash column chromatography. The column was eluted first with hexane (250 mL), giving acenaphthylene **9** as a yellow solid possessing NMR spectroscopic properties identical to those reported by the Brown group.^{2b} ¹H NMR (500 MHz; CDCl₃): δ (ppm) 7.71 (2H, dd, *J* = 8, 1 Hz, H5,6), 7.59 (2H, dd, *J* = 7, 1 Hz, H3,8), 7.44 (2H, dd, *J* = 8, 7 Hz, H4,7), 7.01 (2H, s, H1,2). ¹³C NMR (125 MHz; CDCl₃): δ (ppm) 139.5 (C9,10), 128.1 (C12), 128.0 (C11), 129.2 (C1,2), 127.6 (C4,7), 127.1 (C5,6), 124.0 (C3,8). The column was then treated with a mixture of CH₂Cl₂ in hexane (1:20; 800 mL), giving the dimer of benzopentalene **6** as a yellow oil possessing NMR spectroscopic properties identical to those reported by the Brown group.^{2b} ¹H NMR (500 MHz; CDCl₃): δ (ppm) 7.33–7.21 (4H, s, H1,10; H2,9), 7.18–7.08 (4H, s, H3,8; H4,7), 6.89 (2H, t, *J* = 2 Hz, H11,12), 6.49 (2H, s, H5,6), 3.79 (2H, br d, *J* = 2 Hz, H5a,5b), 3.22 (2H, br d, *J* = 4 Hz, H11a,11b). ¹³C NMR (125 MHz; CDCl₃): δ (ppm) 155.7 (C4a,6b), 151.9 (C4b,6a), 150.1 (C10a,12a), 134.1, 129.8 (C11a,11d), 128.3, 123.6, 122.5, 120.8 (C5,6), 116.7 (C11,12), 58.0 (C5a,5b), 40.8 (C11b,11c).

Acknowledgment. We thank the University of Washington Chemistry Department for generous grants of computer time. This work was funded by the National Science Foundation through grant CHE-0073373. We thank Professor L. T. Scott for useful comments and unpublished results, and Professor Robert A. Pascal, Jr. for helpful advice.

Supporting Information Available: Full experimental details on the synthesis of all labeled materials for pyrolysis. Included for each reported calculated stationary point are Cartesian coordinates (Ångstroms), the CCSD(T)/cc-pVDZ electronic energy (hartrees), the B3LYP/6-311+G** electronic energy (hartrees), symmetry, and, from the B3LYP vibrational analysis, zero-point energy (ZPE) correction (hartrees), thermal correction to enthalpy (hartrees), and lowest energy vibration and its symmetry (negative implies a vibration with an imaginary frequency) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA0213672

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