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Thermal Rearrangements of 2-Ethynylbiphenyl: A DFT Study of Competing Reaction Mechanisms

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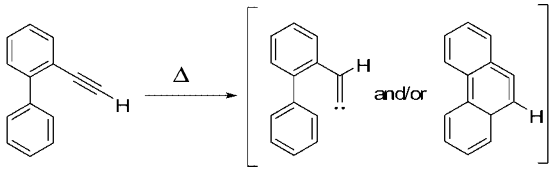
Received October 8, 2008



Mechanistic pathways for high-temperature rearrangements of 2-ethynylbiphenyl have been investigated by calculations at the B3LYP/6-31G(d) level of theory, with free energy estimates at 625 °C. Two different routes for high temperature thermal rearrangement can lead to phenanthrene, which was the major product observed by Brown and co-workers (*J. Chem. Soc. Chem. Commun*. **1974**, 123). 1,2-Hydrogen shift (Hopf type B mechanism) affords a vinylidene which proceeds to the major product by sequential electrocyclic closure and a 1,2-shift, rather than the expected aryl C−H insertion. Alternatively, insertion of the vinylidene into a ring double bond would lead directly to the observed minor product, benzazulene. Along a competitive pathway, electrocyclic closure to an isophenanthrene is predicted to be nearly isoenergetic. This intermediate should have a planar allene structure, with substantial diradical character. Sequential hydrogen shifts lead to phenanthrene but with higher cumulative barriers than for the vinylidene route. Calculation of 625 °C free energies shows that the carbene mechanism is of lower energy, primarily because of the lower entropic cost. Predictions are made for the unusually facile hydrogen atom dissociation from isoaromatics at high temperature, a consequence of aryl radical formation. Isophenanthrene, isobenzene (1,2,4-cyclohexatriene) and several isonaphthalenes are also predicted to have unusually low C−H bond dissociation energies. Potential significance as a source of aryl radicals in high temperature and combustion chemistry is discussed.

Introduction

In 1969, Hopf and Musso reported the thermal rearrangement (Scheme 1) of 1,3-hexadien-5-yne (**1**) to benzene.[1] Mechanistic studies have now demonstrated two competing mechanisms for this common high temperature process.[2] For parent structure **1**, labeling studies and computations[2b,3] support the "Type A" mechanism which begins with electrocyclic closure and proceeds to product by two hydrogen shifts. Other dienyne derivatives favor the "Type B" carbene mechanism which begins with a 1,2-H shift. In 1974, Brown and co-workers presented experimental evidence for the high temperature thermal interconversion of alkynes and vinylidenes.[4] This simple process, now known as the Roger Brown rearrangement, provides a mechanistic basis for numerous complex thermal reactions.[5,6] The accepted type B Hopf mechanism includes a Brown rearrangement step. Vinylidenes such as **4** or **7** must lie in very shallow energy minima.[7] For the thermal rearrangement of 1-naphthylacety-

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(1) Hopf, H.; Musso, H. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 680.

(2) (a) Roth, W. R.; Hopf, H.; Horn, C. *Chem. Ber.* **1994**, *127*, 1765. (b) Prall, M.; Krüger, A.; Schreiner, P. R.; Hopf, H. *Chem.*−*Eur. J.* **2001**, *7*, 4386. (c) Zimmerman, G. *Eur. J. Org. Chem.* **2001**, 457, and references therein.

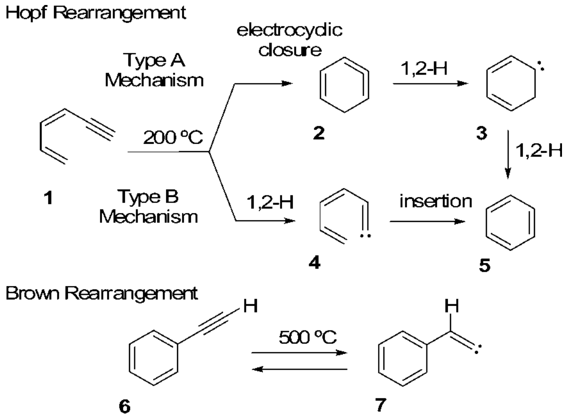
(3) (a) Litovitz, A. E.; Carpenter, B. K.; Hopf, H. *Org. Lett.* **2005**, *7*, 507. (b) Balcioglu, N.; Ozgur Ozsar, A. *THEOCHEM* **2004**, *677*, 125. (c) Dinadayalane, T. C.; Priyakumar, U. D.; Sastry, G. N. *J. Phys. Chem. A* **2004**, *108*, 11433. (d) Rodriguez, D.; Navarro-Vazquez, A.; Castedo, L.; Dominguez, D.; Saa, C. *J. Org. Chem.* **2003**, *68*, 1938.

(4) (a) Brown, R. F. C.; Harrington, K. J.; McMullen, G. L. *J. Chem. Soc., Chem. Commun.* **1974**, *n/a*, 123. (b) Brown, R. F. C.; Eastwood, F. W.; Harrington, K. J.; McMullen, G. L. *Aust. J. Chem.* **1974**, *27*, 2393.

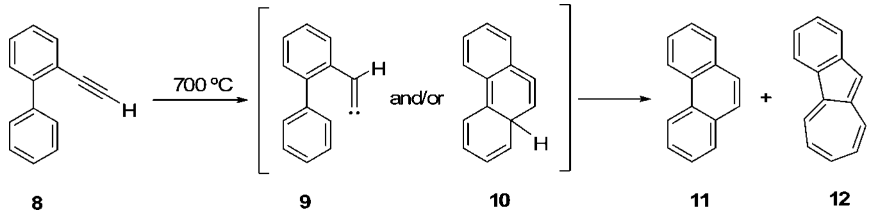
(5) Review: (a) Brown, R. F. C. *Eur. J. Org. Chem.* **1999**, 3211. (b) Mabry, J.; Johnson, R. P. *J. Am. Chem. Soc.* **2002**, *124*, 6497.

10.1021/jo802259h CCC: $40.75 © 2009 American Chemical Society
Published on Web 12/09/2008

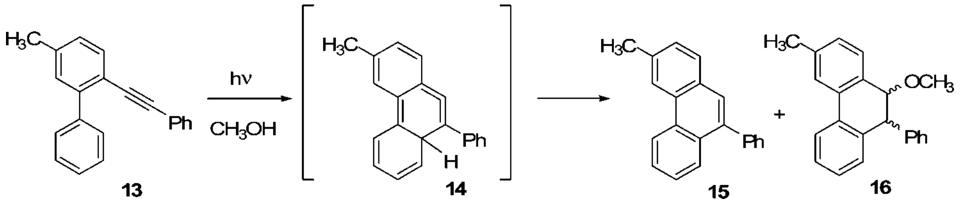
SCHEME 1. Thermal Rearrangements



SCHEME 2. Thermal Rearrangements of 2-Ethynylbiphenyl



SCHEME 3. Photochemistry of a 2-Ethynylbiphenyl



lene to acenaphthylene, computations predict either a one step mechanism or a vinylidene intermediate which lies in a shallow energy minimum.[8] Ring closure has been predicted to occur by insertion of the carbene into an aromatic C−H bond.

The Hopf and Brown rearrangements are among the most commonly observed and synthetically useful processes in the field of high-temperature chemistry.[2,6] Both reactions also figure prominently in mechanisms proposed for aromatic ring formation in hydrocarbon combustion chemistry.[9]

Among commonly cited examples of alkyne thermal chemistry, Brown and co-workers reported in 1974, that vapor phase thermolysis of 2-ethynylbiphenyl (**8**) afforded phenanthrene (**11**) and benzazulene **12** (Scheme 2) in a ratio of 72:28.[4] The accepted Hopf type B mechanism[2,8a] begins with 1,2-shift to **9**, which then inserts into proximate C−H or C═C bonds to afford the two observed products. However, an alternative Hopf type A route to **11** would begin with electrocyclic closure to isophenanthrene **10**, followed by sequential hydrogen shifts. No experimental data distinguishes these two fundamentally different pathways.

Evidence in support of a cyclic allene intermediate comes from recent results by Lewis and co-workers who reported photochemical studies on this chromophore.[10] As one example, irradiation of **13** in methanol resulted in the isolation of **15** and **16** (Scheme 3). The observed products were consistent with the intermediacy of strained cyclic allene **14**[11] which the authors suggested might have either biradicaloid or zwitterionic character.

We recently showed that 1,2,4-cyclohexatriene (**2**) should have a strain energy of 34 kcal/mol.[11d] Isophenanthrene **10** has this structure built in but must also be destabilized by its "isoaromatic" character.[12] In the present work, we have modeled the pathways connecting **8** with its thermal reaction products and we make predictions on the stability and nature of cyclic allene **10**. We also show here that isoaromatic compounds such as **2** and **10** will have unusually low C−H bond dissociation energies and may be precursors to aryl radicals in high-temperature processes.

Computational Methods

All stationary points were optimized at the B3LYP/6-31G(d) level of theory,[13] followed by vibrational frequency analysis. Spartan 04[14] was used for initial calculations, followed by further

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(6) Synthetic applications: (a) Kirmse, W. *Angew. Chem., Int. Ed.* **1997**, *36*, 1165. (b) Scott, L. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 4994. (c) Hopf, H. In *Modern Arene Chemistry*; Astruc, D., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2002; p 169. (d) Tsefrikas, V. M.; Scott, L. T. *Chem. Rev.* **2006**, *106*, 4868–4884.

(7) (a) Kakkar, R.; Pathak, M.; Chadha, P. *Int. J. Quantum Chem.* **2005**, *102*, 189. (b) Xu, D.; Guo, H.; Zou, S.; Bowman, J. M. *Chem. Phys. Lett.* **2003**, *377*, 582. (c) Loh, Z.-H.; Field, R. W. *J. Chem. Phys.* **2003**, *118*, 4037. (d) Bittner, M.; Köeppel, H. *Phys. Chem. Chem. Phys.* **2003**, *5*, 4604. (e) Zou, S.; Bowman, J. M. *J. Chem. Phys.* **2002**, *117*, 5507. (f) O'Connor, J. M.; Friese, S. J.; Tichenor, M. *J. Am. Chem. Soc.* **2002**, *124*, 3506.

(8) (a) Cioslowski, J.; Schimeczek, M.; Piskorz, P.; Moncrieff, D. *J. Am. Chem. Soc.* **1999**, *121*, 3773. (b) Lifshitz, A.; Tamburu, C.; Dubnikova, F. *Proc. Combust. Inst.* **2007**, *31*, 241.

(9) (a) Miller, J. A.; Klippenstein, S. J. *J. Phys. Chem. A* **2003**, *107*, 7783. (b) Melius, C. F.; Miller, J. A.; Evleth, E. M. *Symp. (Int.) Combust., Proc.* **1992**, *24th*, 621.

(10) Lewis, F. D.; Karagiannis, P. C.; Sajimon, M. C.; Lovejoy, K. S.; Zuo, X.; Rubin, M.; Gevorgyan, V. *Photochem. Photobiol. Sci.* **2006**, *4*, 369.

(11) Reviews on cyclic allenes: (a) Johnson, R. P. *Chem. Rev.* **1989**, *89*, 1111. (b) Christl, M. In *Modern Allene Chemistry*; Krause, N., Hashmi, S. K., Eds.; Wiley-VCH Verlag: Weinheim, 2004; Vol. 1, pp 242−356. (c) Balci, M.; Taskesenligil, Y. In *Advances in Strained and Interesting Organic Molecules*; Halton, B., Ed.; JAI Press Inc: Stamford, CT, 2000; Vol. *8*, pp 43−81. (d) Daoust, K. J.; Hernandez, S. M.; Konrad, K. M.; Mackie, I. D.; Winstanley, J., Jr.; Johnson, R. P. *J. Org. Chem.* **2006**, *71*, 5708.

(12) Miller, B.; Shi, X. *J. Am. Chem. Soc.* **1987**, *109*, 578.

(13) (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) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623. (d) Riley, K. E.; Op't Holt, B. T.; Merz, K. M., Jr. *J. Chem. Theory Comput.* **2007**, *3*, 407. (e) Tirado-Rives, J.; Jorgensen, W. L. *J. Chem. Theory and Comput.* **2008**, *4*, 297.

(14) *Spartan 04*; Wavefunction, Inc.: Irvine, CA, 2005.

SCHEME 4. Rearrangement Pathways and Relative Energetics (kcal/mol)

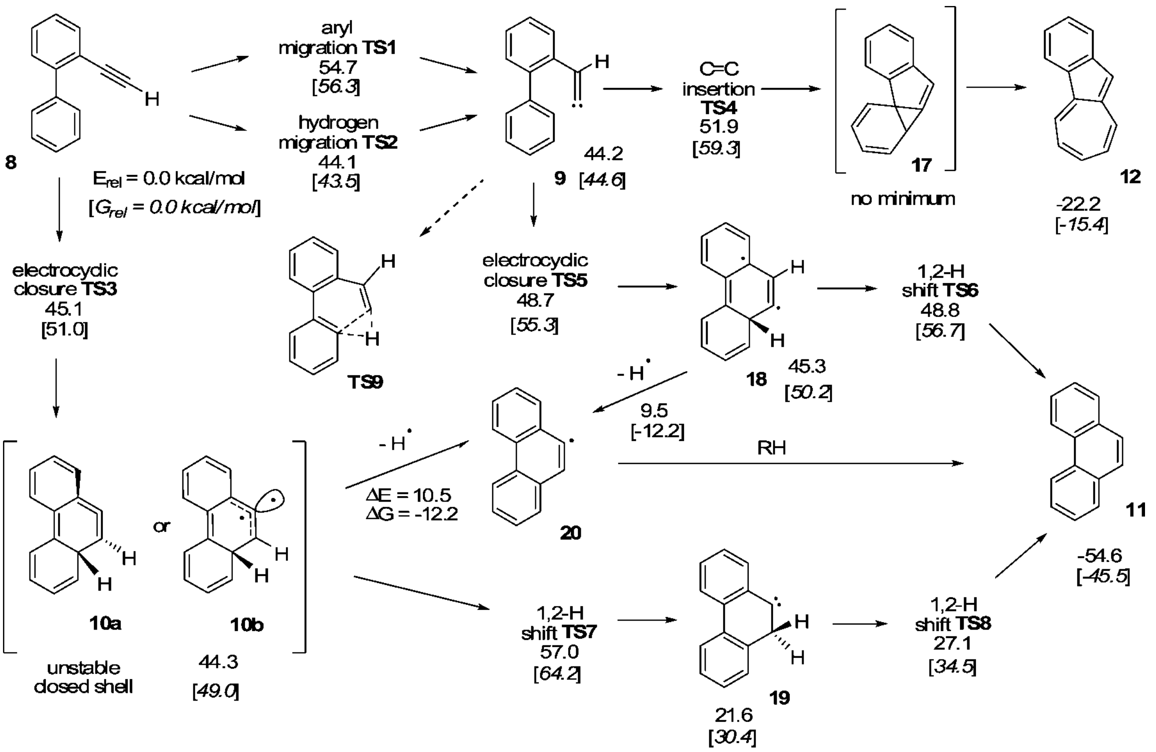

TABLE 1. Energies and Relative Energies of Stationary Points

structure	E_{tot}[a] (hartree)	E_{rel}[a] (kcal/mol)	G_{625}[c] (hartree)	G_{rel}[c] (kcal/mol)
2-ethynylbiphenyl (**8**)	−539.256835	0.0	−539.434850	0.0
benzazulene (**12**)	−539.292259	−22.2	−539.459440	−15.4
phenanthrene(**11**)	−539.343808	−54.6	−539.507338	−45.5
vinylidene (**9**)	−539.186471	44.2	−539.363817	44.6
isophenanthrene (**10b**)[b]	−539.186273	44.3	−539.356795	49.0
diradical (**18**)[b]	−539.184567	45.3	−539.354794	50.2
carbene intermediate (**19**)[b]	−539.221709	21.6	−539.386482	30.4
TS1	−539.169711	54.7	−539.345196	56.3
TS2	−539.186537	44.1	−539.365569	43.5
TS3[b]	−539.185003	45.1	−539.353548	51.0
TS4	−539.174094	51.9	−539.340396	59.3
TS5	−539.179172	48.7	−539.346661	55.3
TS6	−539.179019	48.8	−539.344555	56.7
TS7	−539.166002	57.0	−539.332555	64.2
TS8	−539.213727	27.1	−539.379926	34.5
9-phenanthryl radical (**20**)	−538.669220		−538.835957	
hydrogen atom	−0.500273		−0.540201	
1,2,4-cyclohexatriene (**2**)	−232.018269		−232.133469	
phenyl radical (**21**)	−231.473649		−231.584262	
isonaphthalene **22**[b]	−385.614426		−385.758095	
isonaphthalene **24**[b,d]	−385.581753		−385.728144	
1-naphthyl radical (**23**)	−385.070211		−385.209775	
2-naphthyl radical (**25**)	−385.070421		−385.209963	

[a] B3LYP/6-31G(d) + ZPVE energies (unscaled). [b] Closed shell wave function was unstable: $S^2 > 0$. [c] Free energy calculated at 625 °C. [d] From lowest energy structure. See the Supporting Information.

optimization with Gaussian 03.[15] Intrinsic reaction coordinates (IRC's) were followed for most reactions with Gaussian or GAMESS.[16] Structures that were not obviously closed shell were subjected to a stability check on the wave function. Intrinsic barriers were calculated at the B3LYP+ZPVE level, in addition to a free energy evaluation at 898 K. This second calculation more closely approximates the conditions of flash vacuum pyrolysis.

Results and Discussion

Scheme 4 summarizes the mechanisms we have considered for conversion of **8** to phenanthrene and benzazulene. Predicted relative energies (kcal/mol) and free energies at 625 °C are referenced to starting alkyne **8**. This temperature was chosen

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(15) *Gaussian 03*, Revisions C. and E.01: Frisch, M. J. et al. Gaussian, Inc.: Wallingford, CT, 2004. See the Supporting Information for the full reference.

(16) *GAMESS*: (a) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. J.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347*PC GAMESS*: (b) Granovsky, A. A. PC GAMESS version 7.1, http://classic.chem.msu.su/gran/gamess/index.html.

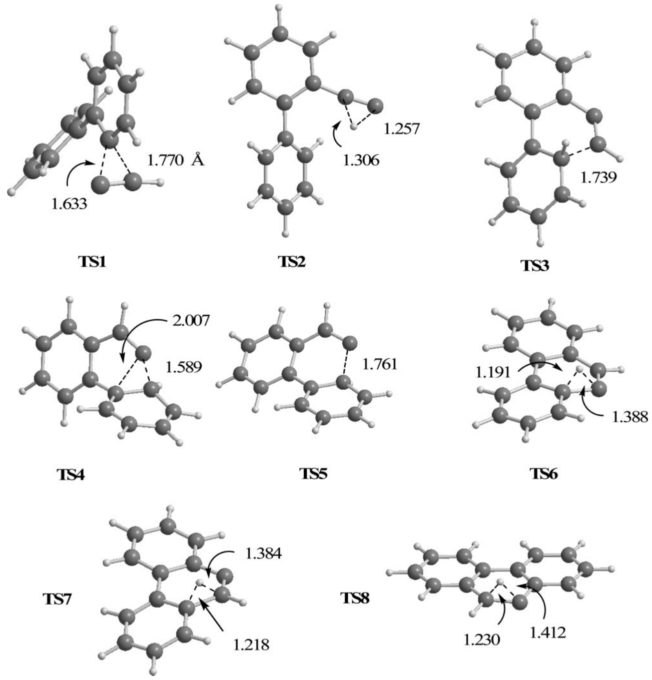
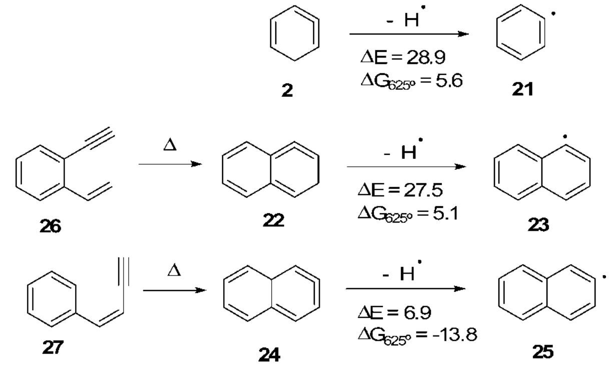


FIGURE 1. B3LYP/6-31G(d)-optimized transition-state structures.

SCHEME 5. Homolytic Bond Dissociation (kcal/mol, 625 °C)



as typical for flash pyrolysis. Transition-state structures are shown in Figure 1, with full data on their energies summarized in Table 1.

Along a type B path, the first mechanistic question is which group would migrate in a Roger Brown rearrangement.[5] Our calculations show that the two routes to vinylidene **9** via **TS1** and **TS2** differ by ca. 10 kcal/mol in predicted barriers; hydrogen migration should thus be strongly favored. With zero point corrections, vinylidene **9** is slightly higher than **TS2**. This is consistent with many previous calculations on vinylidenes which show little or no barrier to rearrangement.[7,8] From **9**, aromatic ring C=C insertion is found to have a modest barrier through **TS4**. No minimum was found for **17**; trial structures opened directly to **12**.

Along the pathway from carbene **9** to phenanthrene, we first explored direct insertion into an aromatic C−H bond. The putative **TS9** structure nearly optimized to normal tolerances for the structure expected for direct insertion. Invariably, full optimization led to lower energy (by ca. 5 kcal/mol) structure **TS5** which is best described as an electrocyclic closure to diradical **18**. Care was taken to choose the correct wave function for this process.

Thus, while **9** and **TS5** have $S^2 = 0$ (i.e., no open shell character), **18** is diradical, with $S^2 = 0.93$. The IRC for this process showed a smooth change in open shell character along the reaction coordinate. From **18**, our calculations predict only a small barrier for rearrangement to **11**; this process is exothermic by nearly 100 kcal/mol.

An alternative route from diradical **18** would be homolytic C−H dissociation to phenanthryl radical **20**, a process that simultaneously generates *three* aromatic rings. The intrinsic barrier is only 10 kcal/mol but the free energy change at 625 °C is −12.2; we conclude that **18** should spontaneously dissociate at high temperature and **20** must then scavenge a hydrogen atom.

Along the competing route, we find that **8** should close to an isophenanthrene through **TS3**. Initial closed-shell calculations afforded chiral allenic structure **10a** but the wave function proved to be unstable. Unrestricted DFT optimization produced **10b** ($S^2 = 0.94$). The intrinsic barrier through **TS3** is only 1 kcal/mol higher than for 1,2-shift but the free energy of activation (51 kcal/mol) is much higher because of the entropic cost of ring formation. Following a Hopf type A mechanism, two hydrogen shifts might lead to **11**. The first shift affords carbene **19** but the predicted barrier is nearly 13 kcal/mol, even though the process is exothermic by 23 kcal/mol. This carbene has diradical character with $S^2 = 0.35$, similar to **3**.[3b] The final shift along this route through **TS8** has a predicted barrier of 5.5 kcal/mol.

Homolytic dissociation from **10b** has similar consequences and energetics to those predicted for **18**. At high temperature, **10b** should dissociate spontaneously, providing a second potential route to **20**. Thus, both cyclization to **10b** and 1,2-shift to carbene **9** provide energetically competitive routes to phenanthrene. Benzazulene **12** is the minor product observed by Brown[4] consistent with a predicted barrier that is several kcal/mol higher along this pathway. No minimum could be located for the putative intermediate **17**.

Isoaromatic Bond Dissociation Energies

Hydrogen atom dissociation is common in high-temperature processes, and there are several points in Scheme 4 where this seems likely. Our predicted C−H dissociation of **10b** suggests that other "isoaromatic" compounds might show similar behavior. To explore the generality of this result, we carried out calculations for isobenzene **2** which has a chiral allenic structure.[3,17] Miller and Melius proposed that allene **2** may be formed by dimerization of propargyl radical in hydrocarbon combustion chemistry and it lies on the pathway to aromatics and soot formation.[9] This might aromatize by the pathways shown in Scheme 1. Alternatively, an entropically favored pathway through C−H dissociation in **2** would give phenyl radical, another flame intermediate. While this has been suggested earlier, the free energy profile was not calculated.[9] Again, we predict a very low bond dissociation energy and a free energy change at 625 °C that is only slightly positive (Scheme 5).

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(17) (a) Musch, P. W.; Scheidel, D.; Engels, B. *J. Phys. Chem. A* **2003**, *107*, 11223. (b) Engels, B.; Schöneeboom, J. C.; Münester, A. F.; Groetsch, S.; Christl, M. *J. Am. Chem. Soc.* **2002**, *124*, 287.

(18) Cyclization of **27** may play a role in diverse thermal chemistry. See: (a) Hofmann, J.; Schulz, K.; Altmann, A.; Findeisen, M.; Zimmermann, G. *Liebigs Ann. Rec.* **1997**, *12*, 2541. (b) Alder, R. W.; East, S. P.; Harvey, J. N.; Oakley, M. T. *J. Am. Chem. Soc.* **2003**, *125*, 5375. (c) Becker, J.; Wentrup, C.; Katz, E.; Zeller, K. P. *J. Am. Chem. Soc.* **1980**, *102*, 5110.

Isonaphthalenes **22** and **25** show similarly low dissociation energies. These might be formed by Hopf cyclization of **26**[2b] and **27**,[3a,18] respectively, although their intermediacy has not yet been proven. We note that, like **10b**, both **22** and **24** have substantial open shell character.

Our results suggest that high-temperature C−H dissociation, driven by the large positive entropy change and formation of aromatic rings, provides an efficient route from isoaromatics to aryl radicals.

Conclusions

Thermal ring closure of ethynylbiphenyl (**8**) to phenanthrene (**11**) might occur by two pathways. We find that predicted barriers for the 1,2-shift (**TS2**) to a vinylidene and electrocyclic closure (**TS3**) to an isophenanthrene (**10b**) are nearly isoenergetic. However, free energy estimates at 625 °C favor the 1,2-shift because of its smaller entropic cost. The major path for this vinylidene (**9**) follows electrocyclic closure to a diradical (**18**), rather than the expected aryl C−H insertion. This intermediate (**18**) can proceed to phenanthrene by sequential hydrogen shifts but seems more likely to undergo spontaneous C−H dissociation, driven by the negative free energy change for this process. The final step would be hydrogen scavenging by phenanthryl radical (**20**). In a competitive process, vinylidene **9** can also insert into the adjacent aryl ring to give benzazulene **12**. This is the minor product, consistent with a higher predicted barrier.

Isophenanthrene lies in a very shallow minimum and should have a diradical (**10b**) rather than a chiral (**10**) structure. This is consistent with photochemical results reported by Lewis and co-workers.[10] Hydrogen atom dissociation from **10b** provides an energetically competitive route to phenanthrene. Finally, we predict that isoaromatic compounds such as isophenanthrene, isonaphthalenes, or isobenzene will have unusually low C−H bond dissociation energies, leading directly to aryl radicals. This process may be important in high temperature and combustion chemistry.

Acknowledgment. Support from the Northrup Grumman Corp. and the Defense Microelectronics Activity (DMEA) is gratefully acknowledged.

Supporting Information Available: Cartesian coordinates and summary energetics for all stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

JO802259H