2532 *J. Org. Chem.* **2002,** *67,* 2532−2540

Substituent Effects in the Interconversion of Phenylcarbene, Bicyclo[4.1.0]hepta-2,4,6-triene, and 1,2,4,6-Cycloheptatetraene

C. Michael Geise and Christopher M. Hadad*

Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210

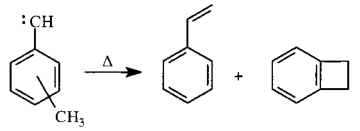
hadad.1@osu.edu

Received October 19, 2001

The effect of aryl substituents on the interconversion of phenylcarbene (**PC**), bicyclo[4.1.0]hepta-2,4,6-triene (**BCT**), and 1,2,4,6-cycloheptatetraene (**CHTE**) has been studied by density functional theory. It is found that substituents have a large effect on both the thermochemistry and activation energy of these rearrangements. For instance, *para*-substitution yields a range of overall activation energies for the formation of **BCT** from **PC** of 20.3 to 11.7 kcal/mol for the NH_2 and NO_2 substituents, respectively. In the *syn-meta*-substituted cases, all of the rearrangements to the substituted **CHTE** species are more exothermic than that of the parent **PC**. The proximity of the substituent to the carbene center can also affect the overall chemistry as in the case of *ortho*-substituted species. Here, formation of bicyclic structures and ylides, which can then rearrange to stable structures, can compete with the ring-expansion process. Also, as calculated herein, the *ortho* substituents can, by a combination of mesomeric and steric interactions with the carbene center, affect the overall barrier to reversible ring expansion. Most notably, in the *anti-ortho*-substituted species, halogens (F and Cl) raise the activation barrier to ring expansion by ∼5 kcal/mol. This is reminiscent of the effect of fluorine substitution on the chemistry (inter- and intramolecular) of phenylnitrene.

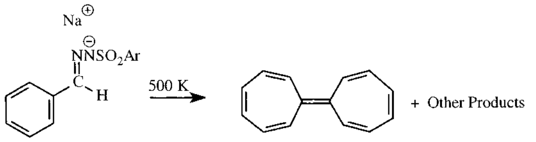
Introduction

Evidence of reversible ring expansion in phenylcarbene (**PC**) was first postulated as being involved in the conversion of tolylcarbenes to styrene and benzocyclobutene.[1,2]

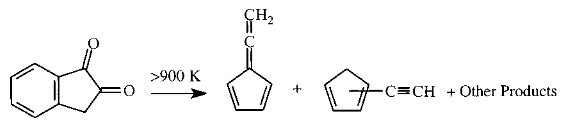


(1)

During this time, there was also a great deal of activity concerning the pyrolysis of putative **PC** (eq 2) and related C_7H_6 precursors (eq 3). These processes show heptafulvalene formation at low temperatures[3] and ring contraction to fulvenallene and ethynylcyclopentadiene at high temperatures.[4]



(2)



(3)

There was even evidence of the reversibility of the ring-expansion process from the organometallic field, where it was observed that deprotonated tropylium-ferrocenyl ions lead to products consistent with ring contraction to the arylcarbene.[5] The rearrangement of **PC** has been the subject of a number of reviews.[6,7]

The mechanism involved in **PC** ring expansion and the products formed by this process were the subject of many debates at the time. The formation of heptafulvalene as the major reaction product was taken as evidence for the intermediacy of cycloheptatrienylidene (**CHT**) in the decomposition of **PC** precursors.[3] Singlet **CHT**, it was proposed, was a particularly stable carbene, as it had an aromatic 6-π electron system,[3] although the

---

* Corresponding author. FAX: (614) 292-1685.

[1] (a) Vander Stouw, G. G.; Shechter, H. *Diss. Abstr.* **1965**, *25*, 6974. (b) Vander Stouw, G. G.; Kraska, A. R.; Shechter, H. *J. Am. Chem. Soc.* **1972**, *94*, 1655.

[2] See, inter alia: (a) Baron, W. J.; Jones, M., Jr.; Gaspar, P. P. *J. Am. Chem. Soc.* **1970**, *92*, 4739. (b) Hedaya, E.; Kent, M. E. *J. Am. Chem. Soc.* **1971**, *93*, 3283. (c) Mayor, C.; Wentrup, C. *J. Am. Chem. Soc.* **1975**, *97*, 7467. (d) Gaspar, P. P.; Hsu, J.-P.; Chari, S.; Jones, M., Jr. *Tetrahedron* **1985**, *41*, 1479.

[3] (a) Joines, R. C.; Turner, A. B.; Jones, W. M. *J. Am. Chem. Soc.* **1969**, *91*, 7754. (b) Wentrup, C.; Wilczek, K. *Helv. Chim. Acta* **1970**, *172*, 1459. (c) Jones, W. M.; Ennis, C. L. *J. Am. Chem. Soc.* **1967**, *89*, 3069. (d) Jones, W. M.; Ennis, C. L. *J. Am. Chem. Soc.* **1969**, *91*, 6391. (e) Mukai, T.; Nakazawa, T.; Isobe, K. *Tetrahedron Lett.* **1968**, 565. (f) Reiffen, M.; Hoffman, R. W. *Tetrahedron Lett.* **1978**, 1107.

[4] (a) Schissel, P.; Kent, M. E.; McAdoo, D. J.; Hedaya, E. *J. Am. Chem. Soc.* **1970**, *92*, 2147. (b) Hedaya, E.; Kent, M. E. *J. Am. Chem. Soc.* **1970**, *92*, 2149. (c) Wentrup, C.; Wentrup-Byrne, E.; Muller, P. *J. Chem. Soc., Chem. Commun.* **1977**, 210.

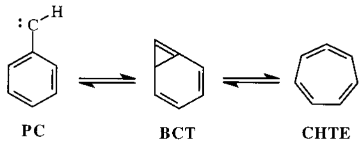
[5] Ashkenazi, P.; Lupan, S.; Schwarz, A.; Cais, M. *Tetrahedron Lett.* **1969**, 817.

[6] (a) Wentrup, C. *Top. Curr. Chem.* **1976**, *62*, 175. (b) Jones, W. M. *Acc. Chem. Res.* **1977**, *10*, 353. (c) Jones, W. M.; Brinker, U. H. In *Pericyclic Reactions*; Marchand, A. P., Lehr, A. E., Eds.; Academic Press: New York, 1977; Vol. 1, Chapter 3, p 149. (d) Wentrup, C. In *Reactive Intermediates*; Abramovich, R., Ed.; Plenum Press: New York, 1980; Vol. 1, Chapter 4, 263. (e) Wentrup, C. *Reactive Molecules*; Wiley-Interscience: New York, 1984, 220. (f) Moss, R. A.; Jones, M., Jr. *Reactive Intermediates*; Wiley: New York, 1985; Vol. 3, p 91. (g) Wentrup, C. In *Methoden der Organischen Chemie (Houben-Weyl)*; Regitz, M., Ed.; G. Thieme: Stuttgart, 1989; Vol. E19b, p 824.

[7] There are a number of reviews in this area. The reader is cautioned that the understanding of the mechanism for ring expansion/contraction of **PC** has been a *developmental* one. Many conflicting reports and mechanisms have been published in the literature through the years, and one would do well to read the literature with this caveat in mind.

10.1021/jo0162181 CCC: $22.00

possibility of cycloheptatetraene (**CHTE**) formation was also recognized.[8]

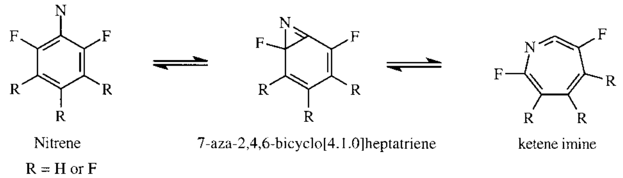


(4)

In their seminal studies, Chapman and co-workers provided spectroscopic evidence of **CHTE** as the product of either flash-vacuum thermolysis (FVT) and matrix photolysis of **PC**[9] and tolylcarbene[10] precursors using matrix isolation techniques. They have also reported several of the chloro- and fluoro-substituted **PC** and **CHTE** derivatives described herein.[9b] Recently, Matzinger and Bally reported the complete UV/VIS and IR spectra of both **PC** and **CHTE**.[11] Interestingly, to date, direct evidence has not been obtained for the existence of bicyclo[4.1.0]hepta-2,4,6-triene (**BCT**), although there have been several product studies characterizing the reactivity of putative **BCT** and related precursors.[12] Studies of benzannelated derivatives, though, do provide direct evidence for the analogous intermediates in the rearrangement of naphthylcarbenes.[13] As well, Miller and Gaspar demonstrated the participation of a **BCT** analogue (as either a short-lived intermediate or transition state) in the rearrangement of cyclohexenylmethylene.[12c]

Recent high-level ab initio theoretical studies on the C_7H_6 potential energy surface have provided details of the **PC** rearrangement that had previously been quite speculative.[14−17] These works provided confirmation of the IR spectrum of Chapman and co-workers assigned to **CHTE**,[14] provided detailed energetic information on the interconversion of a number of the C_7H_6 isomers[15,17] and also presented a detailed characterization of **CHT**.[14−16] Perhaps the most important finding of these works is that the formation of **BCT** is the rate-determining step for this reaction ($E_a \approx 15$ kcal/mol to form **BCT** from **PC**), with the barrier to rearrangement of **BCT** to **CHTE** lying only ~3 kcal/mol above **BCT**. Thus, the failure of previous experimental studies to observe **BCT** as a stable intermediate in the thermolysis or photolysis of **PC** is not surprising. Any molecule with enough energy to traverse the **PC** → **BCT** activation barrier will easily continue along the ring-expansion surface to form **CHTE**, the global minimum on this potential energy surface. It should be appreciated that on the complete C_7H_6 potential energy surface, there are more stable species than **CHTE**, as calculated by others.[15] One of the most exciting recent approaches to studying this process takes place in a hemicarcerand medium.[18]

The effect of aryl substituents on the inter-[19−23] and intramolecular[1,2,3,6,24−29] chemistry of **PC** and analogous aryl-carbenes has been the topic of several experimental efforts. Similar phenylnitrene rearrangements[30] as well as the intramolecular reactivity of several heteroaromatic methylidenes[31,32] have also been studied. In the case of phenylnitrene, fluorination of the aromatic ring has been found to stabilize the 7-aza-2,4,6-bicyclo[4.1.0]-heptatriene (**BCT** analogue) relative to the ketene imine (**CHTE** analogue).[30b−e]



In this paper, we present a density functional theory (DFT)[33] study of the effect of aryl-substituents on the ring-expansion reaction of phenylcarbene. Specifically, the activation barriers and relative energies of substi-

---

[8] (a) Untch, K. Presented at the First International Symposium on the Chemistry of Nonbenzenoid Aromatic Compounds, Sendai, Japan, August, 1970. (b) Jones, W. M. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 325.

[9] (a) West, P. R.; Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1982**, *104*, 1779. (b) McMahon, R. J.; Abelt, C. J.; Chapman, O. L.; Johnson, J. W.; Kreil, C. L.; LeRoux, J.-P.; Mooring, A. M.; West, P. R. *J. Am. Chem. Soc.* **1987**, *109*, 2456.

[10] (a) Chapman, O. L.; McMahon, R. J.; West, P. R. *J. Am. Chem. Soc.* **1984**, *106*, 7976. (b) Chapman, O. L.; Johnson, J. W.; McMahon, R. J.; West, P. R. *J. Am. Chem. Soc.* **1988**, *110*, 501.

[11] Matzinger, S.; Bally, T. *J. Phys. Chem. A* **2000**, *104*, 3544.

[12] (a) Billups, W. E.; Reed, L. E.; Casserly, E. W.; Lin, L. P. *J. Org. Chem.* **1981**, *46*, 1326. (b) Billups, W. E.; Reed, L. E. *Tetrahedron Lett.* **1977**, 2239. (c) Miller, P. C.; Gaspar, P. P. *J. Org. Chem.* **1991**, *56*, 5101.

[13] (a) Chapman, O. L.; McMahon, R. J.; West, P. R. *J. Am. Chem. Soc.* **1984**, *106*, 7973. (b) Chateauneuf, J. E.; Horn, K. A.; Savino, T. G. *J. Am. Chem. Soc.* **1988**, *110*, 539. (c) Albrecht, S. W.; McMahon, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 855. (d) Xie, Y.; Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1997**, *119*, 1370. (e) Bonvallet, P. A.; McMahon, R. J. *J. Am. Chem. Soc.* **2000**, *121*, 10496.

[14] Matzinger, S.; Bally, T.; Patterson, E. V.; McMahon, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 1535.

[15] Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1996**, *61*, 7022.

[16] Schreiner, P. R.; Karney, W. L.; Schleyer, P. v. R.; Borden, W. T.; Hamilton, T. P.; Schaefer, H. F., III. *J. Org. Chem.* **1996**, *61*, 7030.

[17] Patterson, E. V.; McMahon, R. J. *J. Org. Chem.* **1997**, *62*, 4398.

[18] Warmuth, R.; Marvel, M. A. *Chem. Eur. J.* **2001**, *7*, 1209.

[19] Creary, X. *J. Am. Chem. Soc.* **1980**, *102*, 1611.

[20] Tomioka, H.; Suzuki, S.; Izawa, Y. *J. Am. Chem. Soc.* **1982**, *104*, 3156.

[21] Mathur, N. C.; Snow, M. S.; Young, K. M.; Pincock, J. A. *Tetrahedron* **1985**, *41*, 1516.

[22] Sugiyama, M. H.; Celebi, S.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 966.

[23] Admasu, A.; Gudmundsdöttir, A. D.; Platz, M. S. *J. Phys. Chem. A* **1997**, *101*, 3832.

[24] Miller, R. J.; Yang, L. S.; Shechter, H. *J. Am. Chem. Soc.* **1977**, *99*, 938.

[25] Miller, R. J.; Shechter, H. *J. Am. Chem. Soc.* **1978**, *100*, 7920.

[26] Dellacoletta, B. A.; Shechter, H. *Tetrahedron Lett.* **1979**, 4817.

[27] Homberger, G.; Dorigo, A. E.; Kirmse, W.; Houk, K. N. *J. Am. Chem. Soc.* **1989**, *111*, 475.

[28] Murata, S.; Ohtawa, Y.; Tomioka, H. *Chem. Lett.* **1989**, 853.

[29] Kirmse, W.; Konrad, W.; Ozkir, I. S. *Tetrahedron* **1997**, *53*, 9935.

[30] (a) For leading references, see: Borden, W. T.; Gristan, N. P.; Hadad, C. M.; Karney, W. L.; Kemnitz, C. R.; Platz, M. S. *Acc. Chem. Res.* **2000**, *33*, 765. (b) Morawietz, J.; Sander, W. *J. Org. Chem.* **1996**, *61*, 4351. (c) Young, M. J. T.; Platz, M. S. *J. Org. Chem.* **1991**, *56*, 6403. (d) Dunkin, I. R.; Thomson, P. C. P. *J. Chem. Soc., Chem. Commun.* **1982**, 1192. (e) Gritsan, N. P.; Gudmundsdöttir, A. D.; Tigelaar, D.; Zhu, Z.; Karney, W. L.; Hadad, C. M.; Platz, M. S. *J. Am. Chem. Soc.* **2001**, *123*, 1951. (f) Smith, B. A.; Cramer, C. J. *J. Am. Chem. Soc.* **1996**, *118*, 5490. (g) Karney, W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 3347.

[31] (a) Hoffman, R. V.; Orphanides, G. G.; Shechter, H. *J. Am. Chem. Soc.* **1978**, *100*, 7927. (b) Emanuel, C. J.; Shevlin, P. B. *J. Am. Chem. Soc.* **1994**, *116*, 5991. (c) Albers, R.; Sander, W. *J. Org. Chem.* **1997**, *62*, 761. (d) Khasanova, T.; Sheridan, R. S. *J. Am. Chem. Soc.* **2000**, *122*, 8585. (e) Khasanova, T.; Sheridan, R. S. *Org. Lett.* **1999**, *1*, 1091. (f) Khasanova, T.; Sheridan, R. S. *J. Am. Chem. Soc.* **1998**, *120*, 233.

[32] (a) For a recent theoretical study of the relative energy of isomeric carbenes and nitrenes (i.e., phenylnitrene vis á vis 2-pyridylidene), see Kemnitz, C. R.; Karney, W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1998**, *120*, 3499. See references therein for pyridylcarbenes in general. (b) For early references, see: Wentrup, C. *Adv. Heterocycl. Chem.* **1981**, *28*, 231.

[33] (a) Labanowski, J. W.; Andzelm, J. *Density Functional Methods in Chemistry*; Springer: New York, 1991. (b) Parr, R. G.; Yang, W. *Density Functional Theory in Atoms and Molecules*; Oxford University Press: New York, 1989. (c) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.

tuted **PC**, **BCT**, and **CHTE** are presented in light of the dramatic substituent effect observed in the ring expansion of phenylnitrene.

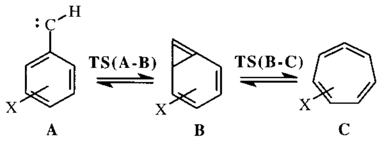
Computational Methods

The geometry of each stationary point was optimized using the three-parameter hybrid functional of Becke for exchange[34] and the gradient-corrected functional of Lee, Yang, and Parr for electron correlation[35] (B3LYP).[36] The 6-31G* basis set[37] was used for these optimizations, and analytical second derivatives were computed to confirm each stationary point by yielding zero imaginary vibrational frequencies for the intermediates and one imaginary vibrational frequency for each transition state. These frequency analyses are known to overestimate the value of the vibrational frequencies, and we therefore scaled the calculated zero-point vibrational energy (ZPE) corrections by 0.9806.[38] Single-point energy calculations were also carried out on the B3LYP/6-31G* geometry using the 6-311+G** basis set[37b] with six Cartesian d functions. The energies reported in the text will correspond to this single-point energy calculation (B3LYP/6-311+G**//B3LYP/6-31G*). All calculations were carried out with the Gaussian 98 suite[39] of programs.

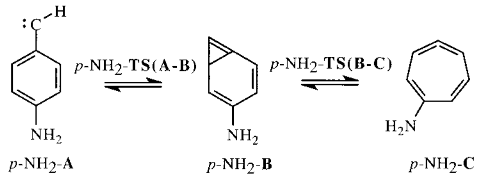
In this paper, the relative energy of each intermediate for the rearrangement of substituted phenylcarbene, X−**PC**, is given with respect to the carbene from which it originated. Each activation barrier is given with respect to the molecule that immediately precedes it on the potential energy surface. The energy reported corresponds to ΔH_0, which includes the electronic energy of the molecule and the scaled zero-point vibrational energy correction obtained from the vibrational frequency analysis.

Results and Discussion

For the sake of clarity, the species in this paper will be referred to in the following manner; *p*-NH_2-**A** will correspond to *p*-aminophenylcarbene, *p*-NH_2-**B**, to the **BCT** analogue, etc.



(5)



(6)

Substituents in the *para*-position of **PC** have been shown to have a large effect on the electronic state of the molecule.[40,41] It has been postulated that this effect originates from a preferential interaction with the empty p orbital of ^{1}**PC**, thus lowering ΔE_{ST} for electron-donating substituents and raising ΔE_{ST} for electron-withdrawing substituents.[40,41] Therefore, since the ring expansion of **PC** is expected to take place on the singlet surface,[42] there should be a parallel effect on the energetics of ring expansion. The experimentally observed product distribution will reflect a combination of intersystem crossing to the triplet state, trapping of intermediates, and ring expansion on the singlet surface. For instance, even though *p*-NO_2-**A** has the lowest barrier to formation of the bicyclo[4.1.0]hepta-2,4,6-triene, *p*-NO_2-**B**, no ring expansion has been experimentally observed in these species.[43] In fact, in the presence of certain trapping agents with which the generated products indicate the reacting electronic state of the carbene, triplet carbene chemistry tends to dominate the observed product distributions for *p*-NO_2-**A**.[44] Aryl substitution may affect each of these processes.[6]

The first point of comparison for our calculations is in **PC** itself. While previous coupled cluster,[14] G2(MP2, SVP)[15] and complete active space[16] calculations predict **BCT** to be slightly lower in energy than **PC**, our results, in agreement with other density functional theory studies,[45] predict **PC** to be lower in energy, though only slightly. This discrepancy is likely due to the difficulty that single determinant methods such as B3LYP have in calculating the energy of strained alkenes such as **BCT**.[46] Despite this shortcoming, DFT methods have been quite successful in the modeling of carbene chemistry and should reproduce energetic trends quite reliably,[47] providing a suitable compromise between the computational accuracy required here and the computing resources necessary to carry out this work for a diverse number of substituents.

Para-Substituted Phenylcarbenes

Substituents in the *para*-position of ^{1}**PC** can display mesomeric interactions with the empty p orbital of the carbene center. Thus, one would expect that electron-donating groups should raise the barrier to ring closure and **BCT** formation, as the transition state for ring

---

[34] (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.

[35] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

[36] Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

[37] (a) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (b) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986.

[38] Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

[39] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, Revision A.7, Gaussian, Inc.; Pittsburgh, PA, 1998.

[40] Karaman, R.; Huang, J.-T. L.; Fry, J. L. *J. Comput. Chem.* **1991**, *12*, 536.

[41] Geise, C. M.; Hadad, C. M. *J. Org. Chem.* **2000**, *65*, 8348.

[42] Carbene intramolecular rearrangements are, in general, believed to take place on the singlet surface, see (a) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1959**, *81*, 5512. (b) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1960**, *82*, 1002. (c) Hine, J. *Divalent Carbon*; Ronald Press: New York, 1964. (d) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1964.

[43] (a) Rothberg, I.; Thornton, E. R. *J. Am. Chem. Soc.* **1964**, *86*, 3302. (b) Abdallah, A. A.; Iskander, Y.; Riad, Y. *J. Chem. Soc. B* **1969**, *9*, 1178.

[44] (a) Goh, S. H. *J. Chem. Soc. C* **1971**, *12*, 2275. (b) Goh, S. H. *J. Chem. Soc., Chem. Commun.* **1972**, *9*, 512. (c) Goh, S. H.; Gian, H. L. *J. Chem. Soc., Perkin Trans. 1* **1979**, *6*, 1625. (d) Creary, X. *J. Am. Chem. Soc.* **1980**, *102*, 1611.

[45] Energies reported correspond to BLYP/6-311+G(3df, 2p)//BLYP/6-31G* + ZPE in ref 15 and B3LYP/6-311+G*//B3LYP/6-31G* + ZPE in ref 16.

[46] Hrovat, D. A.; Borden, W. T. *Mol. Phys.* **1997**, *91*, 891.

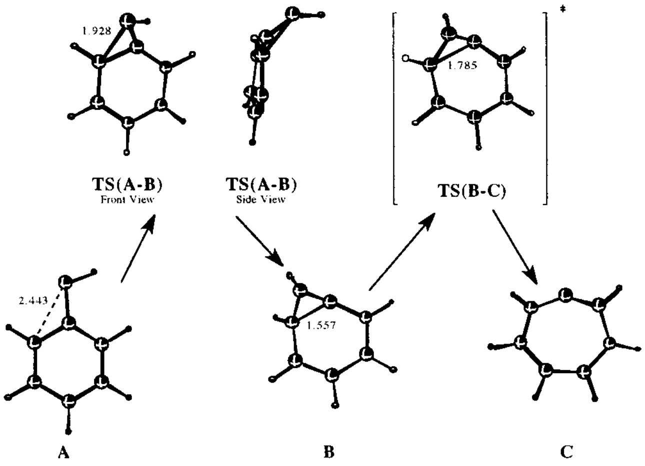


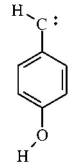
Figure 1. Structure and selected bond distances (in angstroms) of **A**, **B**, and **C** for the parent, **PC**, and the transition states connecting them, calculated at the B3LYP/6-31G* level of theory.

Table 1. Relative Energies (ΔH_0) of Intermediates and Activation Barriers for *Para*-Substituted Rearrangement at the B3LYP/6-311+G Level of Theory**[a]

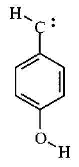
para substituent	σ_p^+	**A**[c]	E_a **TS(A−B)**[c,d]	**B**[c]	E_a **TS(B−C)**[c,e]	**C**[c]
NH_2	−1.111	0.0	20.3	10.5	2.2	−6.2
OH[f]	−0.853	0.0	17.5	6.1	2.4	−8.9
OCH_3[f]	−0.648	0.0	17.2	6.0	3.0	−6.9
CH_3	−0.256	0.0	15.8	3.9	0.9	−11.3
F	−0.247	0.0	16.1	3.1	1.6	−12.5
H	0.000	0.0	14.8	2.1	1.2	−13.6
Cl	0.035	0.0	15.4	2.5	1.4	−12.6
NC	*b*	0.0	14.3	0.9	1.1	−13.7
CF_3	0.582	0.0	12.8	−1.1	1.2	−15.2
CN	0.674	0.0	12.9	−0.7	0.7	−15.1
NO_2	0.740	0.0	11.7	−2.3	0.3	−10.3

[a] Values are given in kcal/mol. [b] σ_p^+ value not available. [c] Fully optimized geometries at the B3LYP/6-31G* level. [d] Activation barrier is relative to **A**. [e] Activation barrier is relative to **B**. [f] Energy reported is for the *anti* rotamer, which has a slightly lower overall activation energy.

closure (Figure 1) involves a large deviation from coplanarity.[14−16,48] This is precisely what is observed, and the relative energies of the relevant stationary points are given in Table 1. Note that in Table 1, only the values for *p*-OH-**A**-*anti* and *p*-OCH_3-**A**-*anti* are given. These refer to the rotamers in which the H−O substituent is oriented opposite to the carbene's C−H bond, for example:

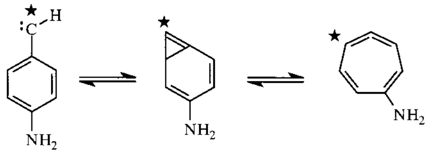


p-OH-**A**-*syn*



p-OH-**A**-*anti*

The rearrangement from the *para*-substituted species gives 5-substituted **CHTE** with the carbene carbon incorporated into the 1-position as shown below (the carbene center is labeled with a star for clarity):



p-NH_2-**A** *p*-NH_2-**B** *p*-NH_2-**C**

(7)

Substitution in the *para*-position by an amino group raises **TS(A−B)** from 14.8 kcal/mol for the parent **PC** to 20.3 kcal/mol for *p*-NH_2-**A**. This observation is exciting in that it (i) demonstrates that the barrier to ring expansion can be controlled by appropriately chosen substituents on **PC** and (ii) provides a possible species for which spectroscopic characterization can be carried out on both the singlet and triplet states. As we demonstrated in an earlier work, the singlet−triplet energy gap in *p*-NH_2-**A** is calculated to be 0.7 kcal/mol (with the triplet being more stable).[41] Given our likely overestimation of the singlet−triplet splitting of the parent **PC** (5.4 kcal/mol gas-phase versus a condensed-phase experimental estimate of 2.3 kcal/mol[22,23,49,50]), it is likely that *p*-NH_2-**A** has a singlet ground state. This leads to the prediction that a judicious choice of aryl-ligand should provide a **PC** derivative that is both hindered toward ring expansion and exists in a detectable equilibrium of singlet and triplet states. Electron-withdrawing substituents lower the **TS(A−B)** energy, and this trend is also consistent with our rationale that the main component of this rate-determining energetic barrier to ring expansion is breaking the conjugation of the singlet carbene's p orbital with the aromatic ring. In fact, there is a relatively smooth energetic decrease in **TS(A−B)** as one increases the electron-withdrawing nature of the *para*-substituent. Table 1 lists substituents in order of their σ_p^+ values.[51] The apparent anomalies in this trend are the halides, *p*-F-**A** and *p*-Cl-**A**, which have **TS(A−B)** values that are 1.3 and 0.6 kcal/mol higher than **PC**, respectively. These larger barriers are likely due to the favorable interaction of the lone pairs on the halogens with the aromatic π-system and the empty p orbital on the carbenic center. Again, we refer to the calculated singlet−triplet energy gap in *p*-F-**A** and *p*-Cl-**A** previously reported,[41] in which the singlet−triplet energy gaps were 4.1, 5.4, and 5.3 for *p*-F-**A**, *p*-Cl-**A**, and **PC**, respectively.

---

(47) (a) Mendez, F.; Garcia-Garibay, M. A. *J. Org. Chem.* **1999**, *64*, 7061. (b) Bettinger, H. F.; Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. F. *In The Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Allinger, N. L., Clark, T., Gasteiger, J., Kollman, P. A., Schaefer, H. F., III, Schreiner, P. R., Eds.; John Wiley and Sons Inc.: Chichester, 1998; pp 183−196. (c) Seburg, R. A.; Hill, B. T.; Squires, R. R. *J. Chem. Soc., Perkin Trans. 2* **1999**, *11*, 2249. (d) Armstrong, B. M.; McKee, M. L.; Shevlin, P. B. *J. Org. Chem.* **1998**, *63*, 7408. (e) Hu, J.; Hill, B. T.; Squires, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 11699. (f) Poutsma, J. C.; Nash, J. J.; Paulino, J. A.; Squires, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 4686. (g) Xie, Y.; Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1997**, *119*, 1370. (h) Gleichmann, M. M.; Doetz, K. H.; Hess, B. A. *J. Am. Chem. Soc.* **1996**, *118*, 10551. (i) Sulzbach, H. M.; Platz, M. S.; Schaefer, H. F., III; Hadad, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 5682. (j) Bettinger, H. F.; Schleyer, P. v. R.; Schreiner, P. R.; Schaefer, H. F., III In *Modern Electronic Structure Theory and Applications to Organic Chemistry*; Davidson, E. L., Ed.; World Scientific Press Inc.: Singapore, 1997; pp 89−171. (k) Farlow, R. A.; Thamattoor, D. M.; Sunoj, R. B.; Hadad, C. M. *J. Org. Chem.*, submitted.

(48) For some discussion on the energetics of rotation about the exocyclic C−C bond in **PC**, see: (a) Dorigo, A. E.; Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1989**, *111*, 6942. (b) Cramer, C. J.; Dulles, F. J.; Falvey, D. E. *J. Am. Chem. Soc.* **1994**, *116*, 9787.

(49) Admasu, A.; Platz, M. S.; Marcinek, A.; Michalak, J.; Gudmundsdöttir, A. D.; Gebicki, J. *J. Phys. Org. Chem.* **1997**, *10*, 207.

(50) This estimate is based upon the surface-crossing mechanism suggested by Griller, Nazran, and Scaiano: Griller, D.; Nazran, A. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 198.

(51) Swain, C. G.; Lupton, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 4328.

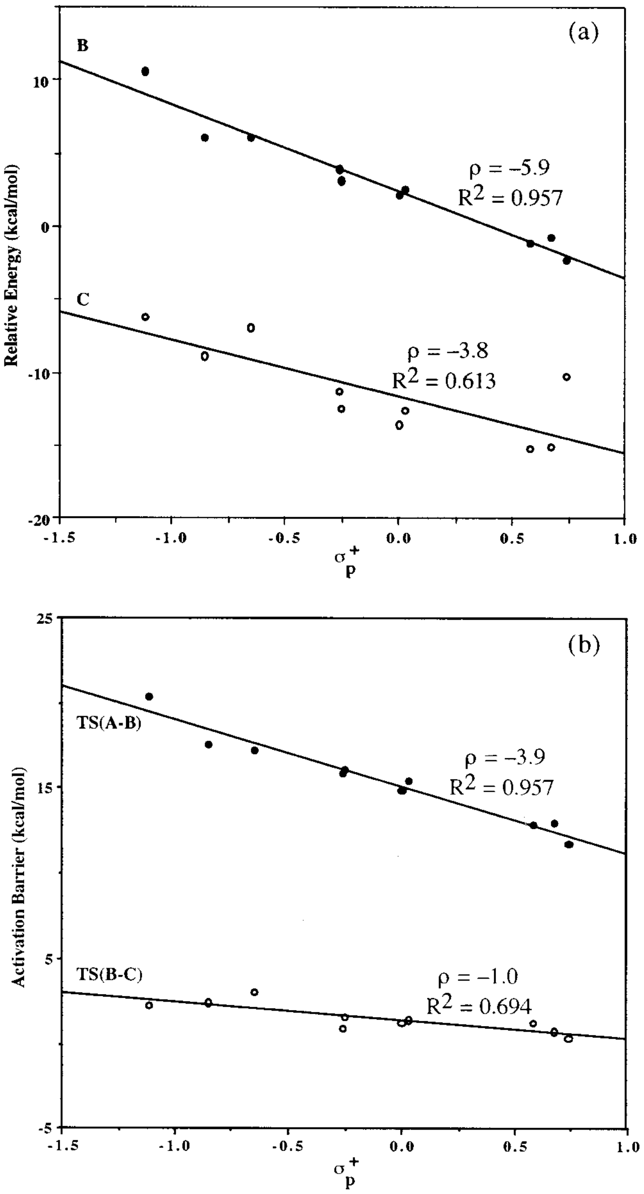


Figure 2. LFE relationship of (a) the relative energy of **B** and **C** and (b) the activation barriers separating **B** and **C** from **A** and **B**, respectively, calculated at the B3LYP/6-311+G**// B3LYP/6-31G* level of theory.

It was also shown that the dominant origin of this substituent effect was interaction with the singlet carbenes. We see the same phenomenon here and its effects on the rearrangement of **PC**. The large effect of fluorine is likely due to the effective orbital overlap of the 2p lone pair electrons from fluorine with the 2p orbital on the aromatic carbon. Chlorine, on the other hand, must interact with the carbon via a 3p orbital, which is less efficient due to the size difference between the more diffuse 3p orbital and the 2p orbital on the aromatic ring carbon, thus the effect on the barrier for rearrangement, **TS(A−B)** is attenuated.

To illustrate the effect of *para* substitution on the rate-determining step, **TS(A−B)**, we have carried out a linear free energy (LFE) analysis[52] on the *para*-substituted species (Figure 2). A good correlation (R^2 = 0.957) is observed in the plot. The slope (ρ value) is −3.9. This effect is similar in magnitude to that observed on the singlet−triplet energy gap of **PC** in which ρ is 5.0.[41] As mentioned earlier, it was established in previous studies[41] that the effect on ΔE_{ST} is primarily due to interaction with the empty p orbital on the carbene center. That a similar effect on energy is seen in **TS(A−B)** in this instance, wherein the transition state, **TS(A−B)**, for rearrangement requires a large deviation from coplanarity, is in complete agreement with our expectations. Also shown in Figure 2 are the LFE plots for **B**, **C**, and **TS(B−C)**. The primary interaction of the aromatic ring with the carbene center takes place via the empty p-orbital on the carbene center. This interaction is not available in **B**; thus, the relative energy of the two species should reflect this substituent interaction with the carbene center. If there is a negligible effect of substitution on the stability of **B** formed, there should be a good linear correlation and the ρ values should be similar for **B** and **TS(A−B)**. However, if there is an effect on the stability of **B** that is qualitatively similar to the effect on **A**, there should be a good linear correlation and ρ should be larger in magnitude for this plot. In fact, there is a good linear correlation (R^2 = 0.957) and a larger ρ value, −5.9 for **B** versus −3.9 for **TS(A−B)**. This stabilizing effect on **B** by electron-donating substituents will become even more evident when we discuss the reaction coordinate diagrams in Figure 3. The activation barrier **TS(B−C)**, however, is referenced to **B**. The plot of this value versus σ_p^+ reflects the stabilizing effect of electron-donating substituents to **B** (negative ρ value), but shows very poor linear correlation (R^2 = 0.694), as one might expect. The relative energy of substituted **C** also shows a poor linear correlation to σ_p^+.

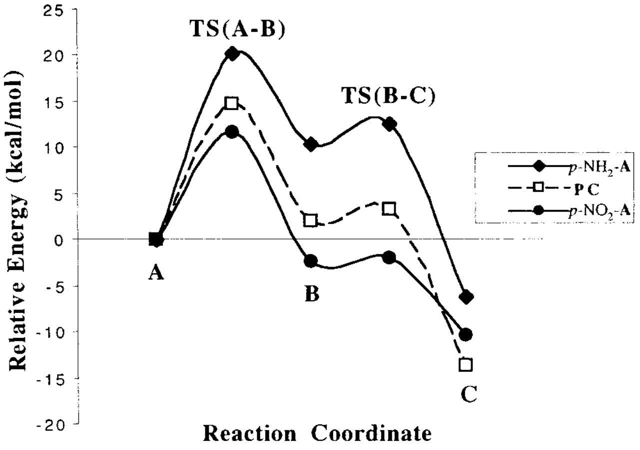


Figure 3. Graphical view of the potential energy surfaces of *p*-NH_2-**A**, **PC**, and *p*-NO_2-**A** calculated at the B3LYP/6-311+G**//B3LYP/6-31G* level of theory.

As mentioned earlier, another interesting observation concerning the effect of *para*-substitution on the **PC** ring-expansion potential energy surface is the relative stability of **B**. In **B**, ring conjugation is lost, and the substituent now plays a much smaller role in stabilization, but an observable one nonetheless. As a result of the interaction with the p orbital on the carbene center in **A**, electron-withdrawing substituents, which served to destabilize **A**, have exothermic rearrangements to **B**. In the extreme case, *p*-NO_2-**A** → *p*-NO_2-**B**, the process is exothermic by 2.3 kcal/mol. Given that DFT underestimates the stability of **BCT** (**B**) in the rearrangement of **PC**,[14−16] this is likely to be an upper limit of the reaction exothermicity.

---

[52] Exner, O. *Prog. Phys. Org. Chem.* **1990**, *18*, 129.

Table 2. Relative Energies (ΔH_0) of Intermediates and Activation Barriers for *Syn-Meta*-Substituted Rearrangement at the B3LYP/6-311+G Level of Theory**[a]

meta substituent	σ_m	**A**[b]	E_a **TS(A−B)**[b,d]	**B**[b]	E_a **TS(B−C)**[b,e]	**C**[b]
NH_2	−0.160	0.0	13.2	1.6	1.6	−18.1
CH_3	−0.069	0.0	14.3	1.9	1.6	−14.9
H	0.000	0.0	14.8	2.1	1.2	−13.6
OCH_3[c]	0.115	0.0	12.9	0.8	2.1	−16.5
OH[c]	0.121	0.0	13.4	1.5	1.5	−17.3
F	0.337	0.0	13.8	1.3	1.1	−17.2
Cl	0.391	0.0	14.2	1.4	1.0	−16.8
CF_3	0.430	0.0	13.8	0.2	1.3	−15.6
NC	*f*	0.0	13.8	0.4	1.0	−16.6
CN	0.560	0.0	13.9	0.0	0.9	−15.9
NO_2	0.710	0.0	13.9	−0.1	0.8	−16.6

[a] Values are given in kcal/mol. [b] Fully optimized geometries at the B3LYP/6-31G* level. [c] Energy reported is for the *syn*-rotamer, which has a slightly lower overall activation energy. [d] Activation barrier is relative to **A**. [e] Activation barrier is relative to **B**. [f] σ_m value not available.

Table 3. Relative Energies (ΔH_0) of Intermediates and Activation Barriers for *Anti-Meta*-Substituted Rearrangement at the B3LYP/6-311+G Level of Theory**[a]

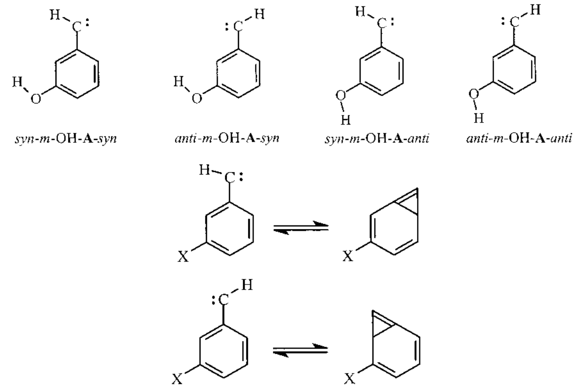
meta substituent	σ_m	**A**[b]	E_a **TS(A−B)**[b,d]	**B**[b]	E_a **TS(B−C)**[b,d]	**C**[b]
NH_2	−0.160	0.0	12.5	−2.2	2.9	−12.6
CH_3	−0.069	0.0	14.0	0.9	2.4	−12.5
H	0.000	0.0	14.8	2.1	1.2	−13.6
OCH_3[c]	0.115	0.0	12.3	−2.5	3.6	−11.9
OH[c]	0.121	0.0	12.8	−2.1	2.4	−13.8
F	0.337	0.0	13.7	−1.2	2.0	−14.9
Cl	0.391	0.0	13.5	−1.7	2.1	−14.2
CF_3	0.430	0.0	13.7	−1.2	2.5	−14.6
NC	*f*	0.0	13.3	−2.2	2.5	−14.8
CN	0.560	0.0	13.3	−2.1	2.2	−15.0
NO_2	0.710	0.0	13.3	−2.6	2.1	−15.4

[a] Values are given in kcal/mol. [b] Fully optimized geometries at the B3LYP/6-31G* level. [c] Energy reported is for the *anti*-rotamer, which has a slightly lower overall activation energy. [d] Activation barrier is relative to **A**. [e] Activation barrier is relative to **B**. [f] σ_m value not available.

Also noteworthy is the fact that the activation barrier for **TS(B−C)** is still much smaller than for **TS(A−B)**. This trend has been observed in previous computational studies.[14−16] The effect of substitution on these potential energy surfaces is shown in Figure 3, which illustrates the reaction profile for *p*-NH_2-**A**, *p*-NO_2-**A** and the parent **PC**. This profile illustrates that electron-donating substituents tend to raise the energy of **TS(B−C)**.

Meta-Substituted Phenylcarbenes

The effect of *meta* substitution on the ring expansion of **PC** is presented in Tables 2 and 3. Again, we would like to clarify our naming convention and choice of which species to report. In the *meta* species, there are two rotations that are important. First is the rotation about the aromatic ring−substituent bond, which typically has a barrier of less than 5 kcal/mol.[53] There is also the rotation about the aromatic ring−carbene bond, which has a much higher barrier (10−15 kcal/mol) and is energetically close to the barrier for ring expansion.[53] Therefore, since rotation about the ipso-carbon carbene−carbon bond is energetically comparable to the barrier (**TS(A-B)**) for ring closure to B, we believe that the rotamer orientation in which the carbene is born will dictate the regiochemistry of ring closure. Since aromatic ring−carbene rotation should be a slow process and aromatic ring-substituent rotation should be quite facile, we will treat the carbene rotamers separately and only report the lower energy pathway for the *meta* substituent rotamer. We should note that the carbene can only undergo ring closure with the bond that is opposite to the carbene H, as shown below. Our naming convention is to give the carbene rotamer designation as a prefix and the substituent rotamer as a suffix:



1. *Syn-Meta*-Substituted PC. Table 2 presents the relative energy of the *syn-meta* species. These are presented in increasing order of σ_m.[54] The most striking feature of these data is the range of **TS(A−B)** energies. Whereas in the *para*-substituted cases, the energetic range was 8.6 kcal/mol, the range for the *meta* cases is only 1.6 kcal/mol. Compare this with the range of the singlet−triplet energy gaps calculated for the *para*- and *meta*-substituted cases, which is 9.6 and 2.6 kcal/mol, respectively.[41] Interestingly, *syn-meta* substitution serves to both lower the activation barrier **TS(A−B)** and, in accordance with Hammond's postulate,[55] lower the relative energy of **B**.

2. *Anti-Meta*-Substituted PC. Table 3 presents the results of *anti-meta* substitution. As in *syn-meta* substitution, all of the **TS(A−B)** energies are lower upon substitution as compared to the prarent **PC**. Here, though, the range is a little larger (2.5 kcal/mol), quite close to the range of singlet−triplet splittings of 2.6 kcal/mol.[41] Also, for these rotamers, all of the rearrangements to **B** are predicted to be exothermic, except for **PC** and *anti-meta*-tolylcarbene. For all of the species, **TS(B−C)** is still quite low; thus the experimental observation of **B** (now a quite exothermic rearrangement given DFT's underestimation of the stability of strained alkenes, see above) is still quite unlikely. The overall rearrangements of the *anti-meta* species are not as exothermic as those of the *syn-meta* species, but in both cases, **C** is by far the most stable species on the portion of the C_7H_5-X potential energy surface studied here.

Ortho-Substituted Phenylcarbenes

The chemistry of *ortho*-substituted **PC** is complicated by the availability of intramolecular rearrangement involving the carbene center and the *ortho* substitu-

---

(53) Geise, C. M.; Hadad, C. M.; Zheng, F.; Shevlin, P. B. *J. Am. Chem. Soc.* **2002**, *124*, 355.

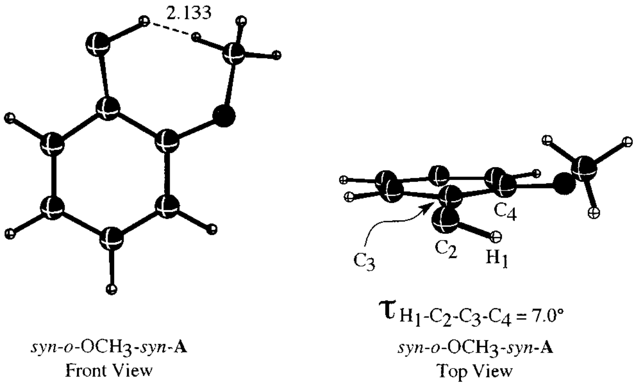
(54) McDaniel, D. H.; Brown, H. C. *J. Org. Chem.* **1958**, *23*, 420.

(55) (a) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334. (b) Leffler, J. E. *Science* **1953**, *117*, 340.

Table 4. Relative Energies (ΔH_0) of Intermediates and Activation Barriers for *Syn-Ortho*-Substituted Rearrangement at the B3LYP/6-311+G Level of Theory**[a]

ortho substituent	**A**[b]	E_a **TS(A−B)**[b,c]	**B**[b]	E_a **TS(B−C)**[b,d]	*C*[b]
NH_2	0.0	17.2	7.3	3.6	−10.4
OH[e]	0.0	15.8	4.5	3.2	−12.5
OCH_3[f]	0.0	11.9	0.2	2.5	−20.3
CH_3	0.0	12.2	0.2	2.2	−16.0
H	0.0	14.8	2.1	0.9	−13.6
F	0.0	16.5	4.6	2.1	−14.3
Cl	0.0	13.5	1.2	1.8	−17.1
CF_3	0.0	10.6	−2.9	1.2	−19.3
CN	0.0	12.7	−0.7	1.2	−16.4
NC	0.0	13.9	1.3	1.9	−15.3

[a] Values are given in kcal/mol. [b] Fully optimized geometries at the B3LYP/6-31G* level. [c] Activation barrier is relative to **A**. [d] Activation barrier is relative to **B**. [e] Energy reported is for the *anti*-rotamer, which has a lower energy. [f] Energy reported is for the *syn*-rotamer, which has a lower energy.



syn-o-OCH_3-*syn*-**A** Front View

syn-o-OCH_3-*syn*-**A** Top View

Figure 4. Structure and selected geometric parameters (distance in angstroms, angle in degrees) of *syn-o*-OCH_3-*syn*-**A** calculated at the B3LYP/6-31G* level of theory.

Table 5. Relative Energies (ΔH_0) of Intermediates and Activation Barriers for *Anti-Ortho*-Substituted Rearrangement at the B3LYP/6-311+G Level of Theory**[a]

ortho substituent	**A**[b]	E_a **TS(A−B)**[b,c]	**B**[b]	E_a **TS(B−C)**[b,d]	**C**[b]
OCH_3[e]	0.0	16.0	−1.1	0.6	−17.9
CH_3	0.0	17.2	2.1	1.0	−14.6
H	0.0	14.8	2.1	1.7	−13.6
F	0.0	19.8	−6.5	3.1	−18.2
Cl	0.0	19.6	−7.5	3.1	−18.8
CF_3	0.0	12.8	−7.9	3.4	−19.9
CN	0.0	14.0	−3.0	1.2	−17.7
NC	0.0	18.2	−3.6	1.4	−18.1

[a] Values are given in kcal/mol. [b] Fully optimized geometries at the B3LYP/6-31G* level. [c] Activation barrier is relative to **A**. [d] Activation barrier is relative to **B**. [e] Energy reported is for the *anti*-rotamer, which has a lower energy.

ent.[56,57] As discussed earlier, this is aptly illustrated in the formation of styrene and benzocyclobutene from the tolylcarbenes.[1,2] In this section, we will only discuss our computational findings regarding the energetics of the ring-expansion reaction for the *ortho* isomers. Recently, we have studied in more detail the intramolecular reactions of methoxy-substituted **PC** both computationally and experimentally.[53]

1. *Syn-Ortho*-Substituted PC. Table 4 summarizes the relative energy of the stationary points involved in the expansion of *syn-ortho*-substituted **A**. Several factors, including resonance stabilization of the singlet **A**, hydrogen-bonding and steric destabilization of the reacting carbene contribute to the observed activation barriers to rearrangement. These factors converge to provide a picture that is quite different from the mesomerically similar *para* isomers. For instance, in *syn-o*-NH_2-**A** (Table 4), the overall barrier to rearrangement is 17.2 kcal/mol (vis á vis 14.8 kcal/mol for **PC**). The explanation here is that preferential resonance stabilization of the starting carbene that does not contribute to stabilizing the out-of-plane transition state results in a higher activation barrier (Figure 1). In the case of *syn-o*-OCH_3-**A**-*syn*, which should also provide resonance stabilization to the empty p-orbital of the carbene, the activation barrier is 11.9 kcal/mol, which is 2.9 kcal/mol lower than in **PC**. This is likely due to destabilization of the carbene via steric repulsion between the methoxy group and the carbene (Figure 4) which forces the $H_1{-}C_2{-}C_3{-}C_4$ dihedral angle between the carbene C−H bond and the aromatic ring to be 7.0° out of plane. In fact, the complete rearrangement of *syn-o*-OCH_3-**A**-*syn* to *syn-o*-OCH_3-**C**-*syn* is much more exothermic (7.8 kcal/mol) than that of the structurally similar *syn-o*-OH-**A**-*anti*. This is a reasonable result if there is a large degree of steric interaction of the carbene with the *ortho*-substituent.

Electron-withdrawing substituents, such as CF_3, lower the barrier to ring closure to **BCT** compared to **PC**. *Syn-o*-CF_3-**A** has a barrier to rearrangement of 10.6 kcal/mol, which is 4.2 kcal/mol lower than in **PC**. Again, this is probably due to a combination of electronic and steric destabilizing interactions with the carbene center accompanied by a relatively small interaction in the transition state. The electron-withdrawing effect should be much smaller in the *ortho* position, as inductive effects are not as strong owing to the ~60° dihedral angle between the ring C-carbene C and ring C-substituent bonds as opposed to a corresponding 180° angle in the *para*-substituted species. Evidence that this is mainly a steric effect can be inferred from the results for *anti-o*-CN-**A**. Here, steric interaction with the carbene center should be quite small, as CN is a linear substituent. In such a case, electron-withdrawing effects are expected to be the major contributor to activation energy differences and the barrier is only lowered by 2.1 kcal/mol.

2. *Anti-Ortho*-Substituted PC. The relative energetics of the *anti-o*-X-**A** potential energy surface for ring expansion are given in Table 5. For both the NH_2- and OH-substituted species, 1,4-H-migration complicates the ring-expansion process.[41] Therefore, we do not report findings on the *ortho*-substituted NH_2 and OH species here.

The overall activation barrier for the ring closure with every substituent, given by **TS(A−B)**, is larger for the *anti-o*-X-**A** isomer than for the *syn-o*-X-**A** isomer (Table 6). Thus, ring expansion toward the *ortho*-X substituent always has a larger activation barrier for rearrangement than away from the substituent. This result can be rationalized by the dominant effect that geometric deformation has on the energetics of this process in which movement of the *ortho* substituent (X) requires some distortion energy in the transition state. This explanation is further supported by the fact that both electron-donating and electron-withdrawing substituents raise the **TS(A−B)** energy of the *anti-ortho* species relative to **A**

---

(56) See, for instance, refs 27, 28, and 29 and references therein.

(57) Sander, W.; Morawietz, J. *Tetrahedron* **1993**, *34*, 1913.

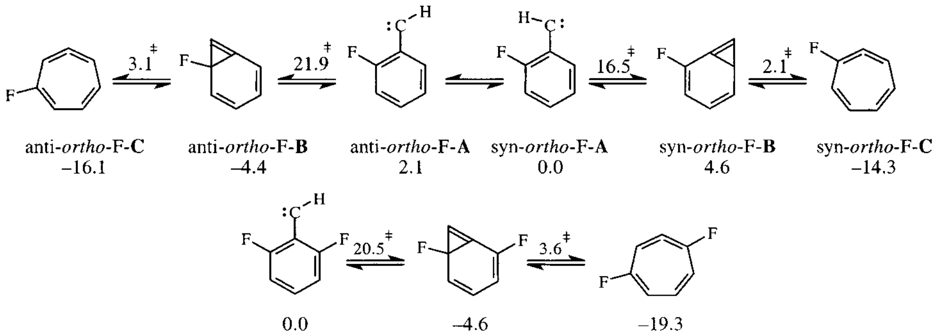


Figure 5. Comparison of *ortho*-fluoro- and *ortho*-difluoro-**PC** potential energy surfaces (ΔH (0K), kcal/mol). The *ortho*-difluoro-**PC** energies are from fully optimized structures at the B3LYP/6-311+G** level of theory. All mono-fluorinated energies are given relative to the *anti-ortho*-F-**PC** isomer which is denoted as zero. Each activation barrier is relative to the reactant's energy for that specific step.

Table 6. Comparison of the Relative Energies (ΔH_0) of the Activation Barriers for Ring Expansion for *Syn-Ortho*- and *Anti-Ortho*-Substituted PC at the B3LYP/6-311+G Level of Theory**[a]

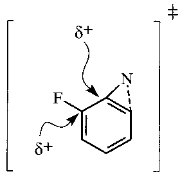
ortho substituent	E_a **TS(A−B)**[b,c] *syn-ortho*-**A** carbenes	E_a **TS(A−B)** *anti-ortho*-**A** carbenes
OCH_3	11.9[d]	16.0[e]
CH_3	12.2	17.2
H	14.8	14.8
F	16.5	19.8
Cl	13.5	19.6
CF_3	10.6	12.8
CN	12.7	14.0
NC	13.9	18.2

[a] Values are given in kcal/mol. [b] Fully optimized geometries at the B3LYP/6-31G* level. [c] Activation barrier is relative to **A**. [d] Energy reported is for the *syn*-rotamer, which has a lower energy. [e] Energy reported is for the *anti*-rotamer, which has a lower energy.

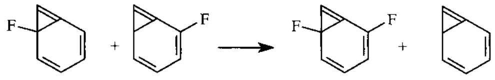
compared to their *syn-ortho* counterparts (Table 6). This effect gives rise to some very interesting results. For instance, the effect of *syn*-halogen substitution on the ring-expansion activation energy for both fluorine and chlorine substitution is raised by ~5 kcal/mol from **PC**. This is actually a much *larger* effect than is observed in the *para*-substituted species. Also, the rearrangement to **B** for each is quite exothermic and moreover, further ring expansion (**TS(B−C)**) has a barrier of 3.1 kcal/mol. The **TS(B−C)** barrier for the halogens is surpassed only by **TS(B−C)** for *anti-o*-CF_3-**A**. The origin of this effect is likely the stabilization of the cyclopropene ring by fluorine substitution (see below).[30g,58] This result is reminiscent of the effect of fluorine-substitution on the ring-expansion of phenylnitrene.[30,59]

3. *Ortho*-Difluoro-Substituted PC. As mentioned earlier, difluoro substitution has a large effect on the relative energies of the various species on the phenylnitrene ring-expansion potential energy surface. In addition to the monosubstituted aryl species studied herein, we have also calculated the energetics for ring expansion of *ortho*-difluoro-**PC** in order to compare substituted **PC** to phenylnitrene. Figure 5 summarizes the relative energies of the monofluoro- and difluorophenylcarbene rearrangement processes.

Interestingly, the rearrangement of *anti-ortho*-F-**A** to *anti-ortho*-F-**B** is exothermic by 6.5 kcal/mol, whereas for *syn-ortho*-F-**A** to *syn-ortho*-F-**B**, the rearrangement is endothermic by 4.6 kcal/mol. This can be attributed to the stabilizing effect of fluorine substitution on small ring compounds.[30g,58] Also, a hydrogen-bonding interaction of the carbene H with the fluorine substituent in *syn-ortho*-F-**A** stabilizes this rotamer compared to *anti-ortho*-F-**A**. It appears that difluoro substitution does not result in any special effects on the **PC** rearrangement surface as it does with the phenylnitrene surface. This observation is consistent with the hypothesis presented by Gritsan et al.[30e] in which the origin of the fluorine effect in phenylnitrene is rationalized as the result of an unfavorable Coulombic interaction between adjacent carbons in the transition state due to the electronegativity difference between C and N.



In **PC**, there is not a significant electronegativity difference between the carbene carbon and the aryl carbon, and there is no significant *ortho*-fluorine effect in **PC** (apart from the general effect that all substituents, regardless of electronic demand, retard insertion toward the substituent). Indeed, the following isodesmic reaction is nearly thermoneutral (0.2 kcal/mol), which implies that the substituent effects observed individually are approximately additive in the difluoro-**PC** cases.



Conclusions

Gas-phase calculations predict that the reversible ring-expansion reaction of **PC** is sensitive to substituents on the aromatic ring. The effect on the activation barrier for this rearrangement is much larger for *para*

---

(58) (a) Getty, S. J.; Hrovat, D. A.; Xu, J. D.; Barker, S. A.; Borden, W. T. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1689. (b) Wiberg, K. B.; Marquez, M. *J. Am. Chem. Soc.* **1998**, *120*, 2932.

(59) (a) Zhai, H.; Platz, M. S. *J. Phys. Org. Chem.* **1996**, *10*, 22. (b) Gritsan, N. P.; Yuzawa, T.; Platz, M. S. *J. Am. Chem. Soc.* **1997**, *119*, 5059. (c) Gritsan, N. P.; Zhai, H. B.; Yuzawa, T.; Karweik, D.; Brooke, J.; Platz, M. S. *J. Phys. Chem. A* **1997**, *101*, 2833. (d) Marcinek, A.; Platz, M. S.; Chan, S. Y.; Floresca, R.; Rajagopalan, K.; Golinski, M.; Watt, D. *J. Phys. Chem.* **1994**, *98*, 412. (e) Poe, R.; Schnapp, K.; Young, M. J. T.; Grayzan, J.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 5054. (f) Marcinek, A.; Platz, M. S. *J. Phys. Chem.* **1993**, *97*, 12674. (g) Banks, R. E.; Sparkes, G. R. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1964. (h) Abramovitch, R. A.; Challand, S. R.; Yamada, Y. *J. Org. Chem.* **1975**, *40*, 1541. (i) Schuster, G. B.; Platz, M. S. *Adv. Photochem.* **1992**, *17*, 69.

substituents than for *meta* substituents. In fact, *para* substituents ranging from NH_2 to NO_2 yield a range of **TS(A−B)** energies of 20.3 to 11.7 kcal/mol. Such a large substituent effect should be readily observable in the experimental ring expansion/contraction process, and such work would be quite welcome for comparison to the computational results reported here.

Ortho-substituted **PC** ring-expansion is complicated by steric interactions between the proximal substituent and the carbene center, the energetics associated with geometric deformations of substituents relative to H as well as rearrangement processes that can lead irreversibly to bond-insertion products. The latter has, of course, been known since the early days of tolylcarbene chemistry and the observed formation of benzocyclobutene.[1,2]

Halogens have a large effect on the ring-expansion process, particularly in the *anti*-*o*-X-**A** species. The *syn*-halogen species seem to be affected by the steric and hydrogen-bonding interactions of the carbene H and the halogen. In the case of fluorine, which presumably forms better hydrogen bonds than chlorine, the activation barrier is raised by 1.7 kcal/mol relative to **PC**. However, for the larger chlorine substituent, which would not benefit as much from a stabilizing hydrogen-bonding interaction, the activation barrier is lowered by 1.3 kcal/mol relative to **PC**. Thus, when provided spatial proximity, significant interaction of the *ortho* substituent with the carbene center can have a large effect on the activation barrier for ring expansion. This can also lead to bicyclic structures and ylides that eventually rearrange to stable products. Indeed, substitution on the aromatic ring of **PC** has a large effect on the relative energetics of the well-known ring-expansion process.

Acknowledgment. We thank the National Science Foundation for support (CHE-9733457) and the Ohio Supercomputer Center for computational resources. We would also like to express our sincere appreciation to Professor Matthew S. Platz (Ohio State University) for helpful discussions during the preparation of this manuscript.

Supporting Information Available: Calculated energies, enthalpies, free energies, Cartesian coordinates, and harmonic frequencies for all species are available. This material is available free of charge via the Internet at http://www.pubs.acs.org.

JO0162181