Pergamon

Tetrahedron Letters 39 (1998) 1505–1508

TETRAHEDRON
LETTERS

Photolysis of Naphtho[b]cyclopropene. Detection of a Diradical Intermediate[1]

Weitao Pan and Maitland Jones, Jr.*

Department of Chemistry, Princeton University, Princeton, New Jersey 08544 USA

Burak Esat and Paul M. Lahti*

Department of Chemistry, University of Massachusetts at Amherst

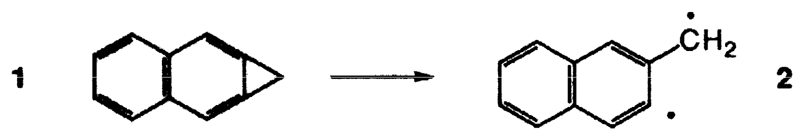
Amherst, Massachusetts 01003 USA

Received 3 December 1997; revised 22 December 1997; accepted 23 December 1997

Abstract: Photolysis of naphtho[b]cyclopropene in hydrocarbons leads to products derived from hydrogen abstraction by a diradical. Photolysis in a cryogenic matrix allows ESR detection of this diradical, which has zero field splitting parameters $D/hc = 0.057$, $E/hc < 0.0002$ cm^{-1}.

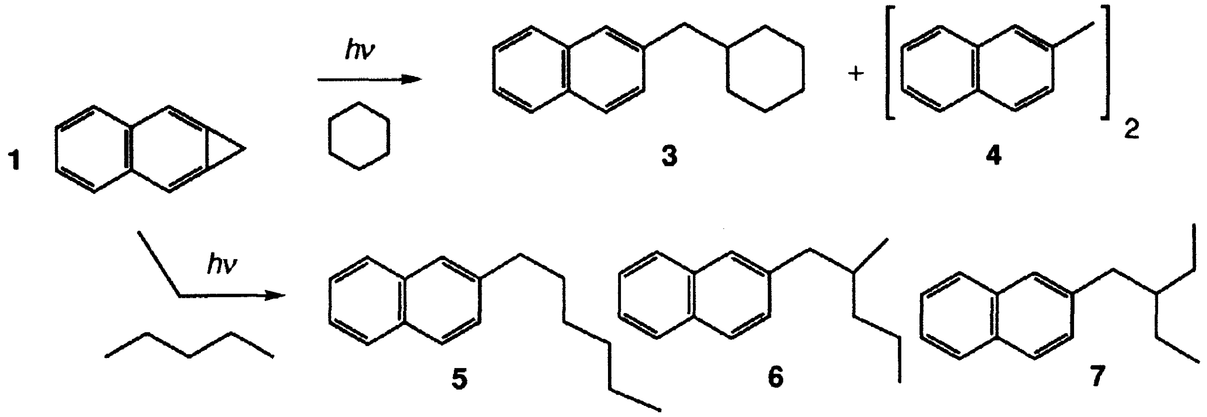
Given their strain energies of ca. 70 kcal/mol,[2] it is no surprise that there is a close connection between benzocyclopropene, naphtho[b]cyclopropene (**1**), and the diradicals formed by breaking of one of the side bonds of the three-membered rings. The closure of such diradicals has been long-implicated in the fomation of these molecules from 3H-indazoles.[3] Moreover, heating or photolysis of cycloproparenes has been shown to lead to the corresponding diradicals. Gas-phase pyrolysis of benzocyclopropene leads to dihydrophenanthrene, a dimer of the putative diradical.[2,4] Pyrolysis of both benzocyclopropene and naphtho[b]cyclopropene leads to ring-contracted compounds that can be rationalized as forming in a sequence of reactions involving diradicals such as **2**.[5] Several examples of capture of the presumed diradicals by internal rearrangement are also known.[6]

PII: S0040-4039(98)00053-7



Closs[3b] *et al.* detected the triplet diradicals formed from a series of 3H-pyrazoles by EPR spectroscopy, and were able to intercept the diradical by trapping with 1,3-butadiene. The same trapping products appeared when benzocyclopropenes were heated to 25 °C in butadiene. Thus, with typical thoroughness, Closs approached the problem from both sides, and provided clear evidence for the intervention of the diradical. Nonetheless, there is neither direct evidence for the presence of a similar diradical in the naphtho[b]cyclopropene series, nor a report of the photochemical production of such a diradical. In this paper we provide both.

Naphthocyclopropene **1** was synthesized by Balci's method,[7] and a degassed solution in cyclohexane was photolyzed in a Pyrex tube with a 450 watt medium-pressure Hanovia mercury arc for 1 hour. Analysis of the products by preparative thin layer chromatography led to the isolation of 29 % of **3**,[8] as well as 10% of **4**.[9] Photolysis in pentane led to three compounds **5**, **6**, and **7**, the spectra of which were consistent with the three radical recombination products shown. Although the compounds were not fully separated, the ^{1}H NMR signals for the α hydrogens (**5**: t, $J = 7.2$ Hz, 2H, **6**: dd, $J = 13.4, 8.0$ Hz, 1H and $J = 13.4, 6.3$ Hz, 1H, **7**: d, J = 7.1 Hz, 2H) allowed us to factor the product mixture into **5**:**6**:**7** = 0.3: 3.4: 1.0. Thus, a secondary hydrogen is about 14 times as reactive as a primary hydrogen, a reasonable value.[10]



Photolysis for 5 min. at 77 K of a solution of 1 in degassed 2-methyltetrahydrofuran with a 1000 watt Pyrex-filtered xenon arc lamp yielded a sample that exhibited the X-band ESR spectrum shown in Figure 1. The spectrum appeared to be persistent for hours under these conditions. Upon thawing of the matrix, the spectral features disappeared irreversibly. In addition to a peak in the g~2 region attributable to radical byproducts of the irradiation, only the spectral features of a triplet state diradical are observed at 2811, 3118, 3692, 4028 (ΔM_S=1 transitions) and 1682 G (ΔM_S=2 transition).

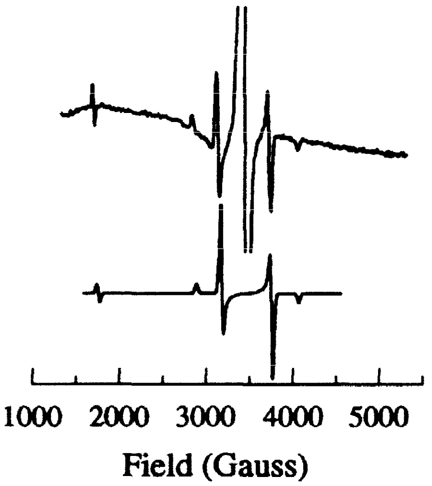
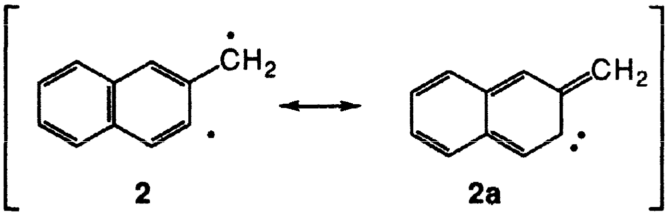
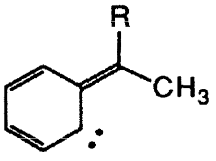


Figure 1. The upper curve is the experimental spectrum obtained at 9.56 GHz at 77 K. The central peak is ascribed to radicals formed in the photolysis. The lower curve is simulated, as described in the text, with D = 0.0556 and E = 0.0004 cm^{-1}.

These spectral features could be fit by lineshape analysis to a triplet state with zero-field splitting (zfs) parameters |D/hc| = 0.0556 cm^{-1}, |E/hc| (0.0004 cm^{-1}. The spectrum was attributed to diradical **2** formed by cyclopropene bond scission. The zfs values are in line with observations for homologous diradicals of type **8**, which share with **2** the structural characteristic that one electron is localized in a sigma-type orbital, whereas the other is delocalized through the molecular pi-system. Diradicals such as **8** have zfs parameters parameters |D/hc| = 0.11-0.12 cm^{-1}, |E/hc| < 0.007 cm^{-1}, depending on the substituent R.[3b] The smaller D-value for **2**, in comparison to that of **8**, is consistent with the greater delocalization of the unpaired pi-electron that can be achieved in the more extensive naphtho[b]cyclopropene system.

The large zfs in diradicals **2** and **8** result from their considerable admixture of carbene-like character. In the resonance formalism, structure **2a** contributes a large one-center interaction between the localized sigma electron and the pi-electron spin density. Since the zfs parameter D is strongly dependent on the dipolar interaction between unpaired electrons, this one-center interaction greatly increases the zfs by comparison to resonance structures in which the electrons are more separated. The trimethylenemethane diradical, with both electrons delocalized in its pi-network, has $|D/hc| = 0.024$ cm^{-1}.[11] Phenylcarbene, with one localized electron and one delocalized electron, has $|D/hc| = 0.515$ cm^{-1} and $E/hc| = 0.025$ cm^{-1}.[12] Diradical **2** has a zfs D value intermediate between these two species, as it has more delocalization of its unpaired pi-electron than does phenylcarbene.





8

References

1. We thank the National Science Foundation for support of this work at Princeton through grant NSF CHE-9322579, and at Massachusetts through CHE-9521594.

2. For reviews of the properties and chemistry of cycloproparenes, see: Halton, B. *Chem. Rev.* **1989**, *89*, 1161. Billups, W. E.; Rodin, W. A.; Haley, M. M. *Tetrahedron* **1988**, *44*, 1305.

3. (a) Anet, R.; Anet, F. A. L. *J. Am. Chem. Soc.* **1964**, *86*, 525. (b) Closs, G. L.; Kaplan, L. R.; Bendall, V. I. *J. Am. Chem. Soc.* **1967**, *89*, 3376. (c) Bambal, R.; Fritz, H.; Rihs, G.; Tschamber, T.; Streith, J. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 668.

4. Halton, B. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 349.

5. Wentrup, C.; Wentrup-Byrne, E.; Müller, P. *J. Chem. Soc., Chem. Commun.* **1977**, 210. Wentrup, C.; Wentrup-Byrne, E.; Müller, P.; Becker, J. *Tetrahedron Lett.* **1979**, 4249.

6. Lüddecke, E.; Rau, H.; Dürr, H.; Schmitz, H. *Tetrahedron* **1977**, *33*, 2677. Halton, B.; Woolhouse, A. D.; Milsom, P. J. *J. Chem. Soc., Perkin Trans. 1*, **1977**, 735.

7. Durucasu, I.; Saracoglu, N.; Balci, M. *Tetrahedron Lett.* **1991**, *32*, 7097. Saracoglu, N.; Durucasu, I.; Balci, M. *Tetrahedron* **1995**, *51*, 10979.

8. Jones, W. M.; Joines, R. C.; Myers, J. A.; Mitsuhashi, T.; Krajca, K. E.; Waali, E. E.; Davis, T. L.; Turner, A. B. *J. Am. Chem. Soc.* **1973**, *95*, 826.

9. Sugimoto, A.; Sakamoto, S.; Suyama, K.; Yoneda, S. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1626.

10. Russell, G. A. Chapter 7 in *Free Radicals*, Vol. 1, Wiley, New York, 1973.

11. Dowd, P. *J. Am. Chem. Soc.* **1966**, *88*, 2587.

12. Wasserman, E.; Trozzolo, A. M.; Yager, W. A.; Murray, R. W. *J. Chem. Phys.* **1964**, *40*, 2408.