

Photochemical Ring Opening of 7-Benzoyl- and 7-Methoxycarbonyldibenzonorcaradienes. Competing 1,2-Hydrogen Shift and Cyclization Reactions of 1,3-Diradicals

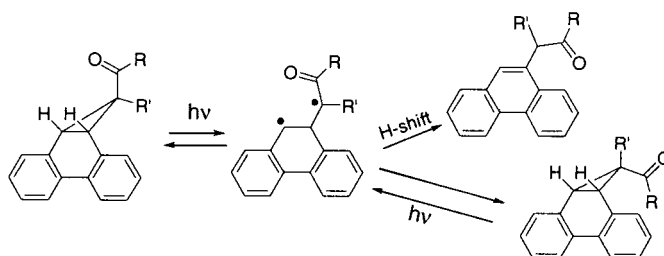
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ABSTRACT

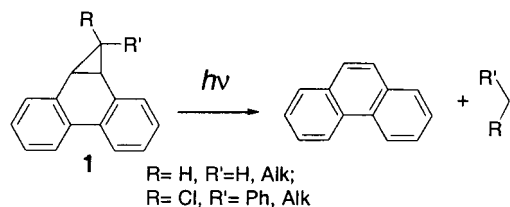


The UV irradiation of dibenzonorcaradienes bearing an acyl or alkoxy carbonyl substituent in the 7-position results in formation of substituted phenanthrenes, as well as *cis*–*trans* isomerization of the starting material. This reaction apparently proceeds via intermediate formation of a short-lived ($\tau = 1$ –20 ns) 1,3-diradical, which is produced by photochemical cleavage of one cyclopropane bond, while no evidence of α -carbonylcarbene formation was found.

The photochemistry of dibenzonorcaradienes has recently attracted substantial attention as it provides a new route for the generation of various carbenes.¹ Irradiation of dibenzonorcaradienes containing halogen or aliphatic substituents in the 7-position of the dibenzonorcaradiene system **1** results in simultaneous cleavage of two cyclopropane bonds and

formation of a corresponding carbene and phenanthrene (Scheme 1).

Scheme 1

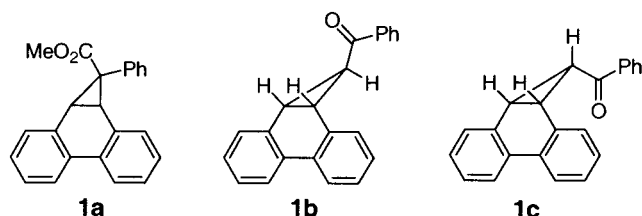


The photochemical behavior of 7-carbonyl-substituted dibenzonorcaradienes (R = CO₂R'' or COR'', Scheme 1), the potential precursors of α -carbonylcarbenes, has not been

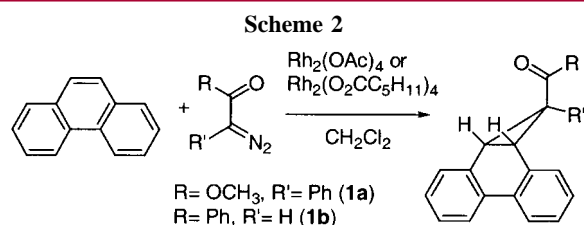
(1) (a) R = Cl, R' = Ph: Nigam, M.; Platz, M. S.; Showalter, B. M.; Toscano, J. P.; Johnson, R.; Abbot, S. C.; Kirchoff, M. M. *J. Am. Chem. Soc.* **1998**, *120*, 8055. (b) R = Cl, R' = Alk: Robert, M.; Likhotvorik, I.; Platz, M. S.; Abbot, S. C.; Kirchoff, M. M.; Johnson, R. *J. Phys. Chem. A* **1998**, *102*, 1507. (c) R, R' = Cl: Chateaufeuf, J. E.; Johnson, R. P.; Kirchoff, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 3217. (d) R, R' = H: Richardson, D. B.; Durret, L. R.; Martin, J. M., Jr.; Putman, N. E.; Slaymaker, S. C.; Dvoretzky, I. *J. Am. Chem. Soc.* **1965**, *87*, 2763. (e) R = H, R' = *t*-Bu: Glick, H. C.; Likhtvorik, I. R.; Jones, M., Jr. *Tetrahedron Lett.* **1995**, *36*, 5715. (f) R, R' = Alk: Lewis, S. M.; Hernandez, S.; Abbot, S. C.; Kirchoff, M. M.; Johnson, R. P. *Abstracts of Papers*, 220th Meeting of the American Chemical Society; American Chemical Society: Washington, DC, 2000; ORGN-372.

explored so far. Such nondiazo sources of the α -carbonyl carbenes could help to define the role of carbene intermediates in the photochemical Wolff rearrangement of α -diazo-carbonyl compounds. These precursors also can become a valuable alternative to thermally unstable diazo-based photoresist in short-wavelength microlithography and other applications.² However, only few attempts at the photochemical generation of α -carbonyl carbenes from non-nitrogenous precursors have been reported. The close relative of 7-carbonyl-substituted dibenzonorcaradienes, 7-carbomethoxybenzonorcaradiene, produces ethoxycarbonyl-carbene upon UV irradiation but in rather low yield (8–11%).³ Platz and coauthors recently observed generation of carbomethoxychlorocarbene in the photodecomposition of the chlorocarbomethoxy-substituted analogue of norcaradiene, methyl 8-chloro-3a,7a-methanoindan-8-carboxylate.⁴

This report describes investigation of the photochemistry of three carbonyl-substituted dibenzonorcaradienes: an ester, 7-methoxycarbonyl-7-phenyldibenzonorcaradiene (**1a**), and two stereoisomeric ketones, *trans*- (**1b**) and *cis*- (**1c**) 7-benzoyldibenzonorcaradiene.



The dibenzonorcaradienes **1a** and **1b** were prepared by rhodium-catalyzed cyclopropanation of phenanthrene with corresponding α -diazocarbonyl compounds (Scheme 2).⁵



It is interesting to note that this reaction is stereospecific, producing only one isomer of 7-acyldibenzonorcaradienes, as evidenced by only one set of signals in the 1H and ^{13}C NMR spectra of compounds **1a** and **1b** and one peak on

(2) (a) For example: Moreau, W. M. *Semiconductor Lithography*; Plenum Press: New York, 1988. Reiser, A. *Photoreactive Polymers: The Science and Technology of Resists*; Wiley: New York, 1989. Reichmanis, E.; Thompson, L. F. *Chem. Rev.* **1989**, 89, 1273. (b) Yang, Y.; Huang, S.; He, H.; Mau, A. W. H.; Dai, L. *J. Am. Chem. Soc.* **1999**, 121, 10832.

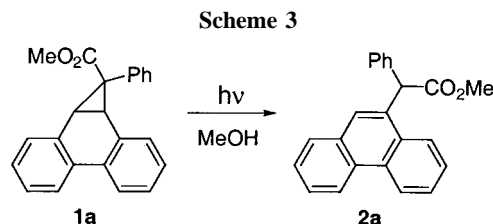
(3) (a) Ciganek, E. *J. Am. Chem. Soc.* **1967**, 89, 1458. (b) Swenton, J. S.; Krubsack, A. J. *J. Am. Chem. Soc.* **1969**, 91, 786.

(4) Likhovorik, I.; Zhu, Z.; Tae, E. L.; Tippmann, E.; Platz, M. S. *J. Am. Chem. Soc.* **2001**, 123, in press.

(5) The preparation procedures for the compounds of **1a**, **1b**, and **1c**, the spectral data for these compounds, and details of photolyses of **1a**, **1b**, and **1c** are provided in the Supporting Information.

HPLC, as well as GC–MS chromatograms. X-ray analysis of **1b** showed *trans* (or *exo*) configuration.⁵

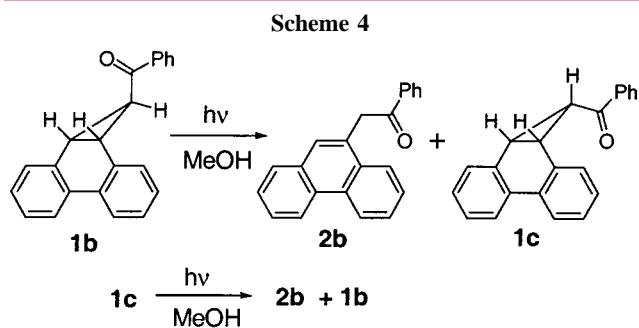
The irradiation of methanolic solution of 7-methoxycarbonyl-7-phenyldibenzonorcaradiene (**1a**) with 300 nm light results in formation of methyl 2-(9-phenanthryl)-phenylacetate (**2a**, Scheme 3).⁵ Small amounts of similar ring-



opening products were also found in complex reaction mixtures of 7-carbomethoxybenzonorcaradiene photolysis.^{3b} In this case, however, **2a** is the only product detected by HPLC.

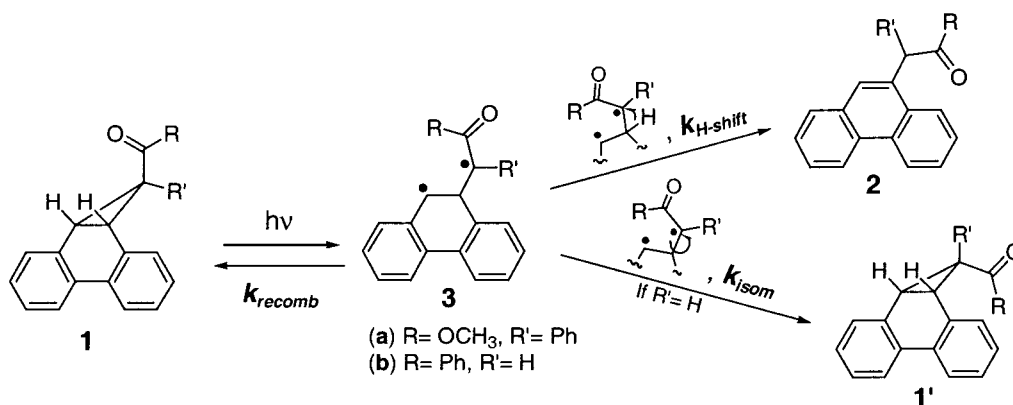
The absence of detectable amounts of phenanthrene and methyl 2-methoxy-2-phenylacetate, the expected product of carbene reaction with the solvent, indicates that photolysis of **1a** does not produce carbomethoxyphenyl-carbene.

Photolysis of *cis*-7-benzoyldibenzonorcaradiene (**1b**) in methanol produces two products, *o*-(9-phenanthryl) acetophenone **2b** and *cis*-7-benzoyldibenzonorcaradiene **1c**, the *cis*(*endo*)-isomer of the starting material (Scheme 4), while no benzoylcarbene-derived products were detected.



Stereoisomeric dibenzonorcaradienes **1b** and **1c** are easily distinguished by the signals of cyclopropane protons in the 1H spectra. Resonance of the proton at the 7-position of norcaradiene system in the *trans* isomer (**1b**) lies in an unusually high field (δ 2.12 ppm) as a result of the shielding effect of two aromatic rings. The same proton is directed away from the aromatic system in the *cis* isomer (**1c**) and gives a signal more than 1 ppm downfield (δ 3.21 ppm). In addition, spin coupling of this proton with two other protons at the cyclopropane ring is much stronger in the *cis* system (**1c**, $J = 9.1$ Hz) than in the *trans* (**1b**, $J = 3.6$ Hz). The latter data agrees well with known values for *cis* and *trans* spin–spin coupling in 2,3-diphenyl-1-acetyl cyclopropanes.⁶ Exhaustive irradiation of the methanolic solution of **1b** resulted in formation of **2b** as the only significant product.

Scheme 5



Photolysis of *cis*-benzoyldibenzonorcaradiene **1c** results in formation of 9-substituted phenanthrene **2b** and isomerization into the *trans*-isomer **1b** (Scheme 4). As in previous cases, no carbene products were detected. These observations suggest that photodecomposition of both isomeric dibenzonorcaradienes **1b** and **1c** proceeds through the same intermediate.

The formation of 9-substituted phenanthrenes **2a** and **2b** in the photolysis of dibenzonorcaradienes **1a–c**, as well as reversible photoisomerization of **1b** and **1c**, can be accommodated by the reaction mechanism shown in Scheme 5.

The excitation of dibenzonorcaradienes **1a–c** results in cyclopropane ring opening and formation of 1,3-diradicals **3a** or **3b**. The decay of the latter can follow three pathways: recombination of radical centers to regenerate starting material (k_{recomb}); 1,2-hydrogen shift to produce 9-substituted phenanthrenes **2a** or **2b** ($k_{\text{H-shift}}$); and isomerization (k_{isom}), which apparently proceeds by rotation about a single bond in the 1,3-diradical intermediate **3b** followed by cyclization. Such rotation is apparently restricted in the diradical **3a** as GS/MS and HPLC monitoring of **1a** photolysis at different levels of conversion found only starting material and substituted phenanthrene **2a**.

The parent 1,3-diradical, trimethylene, is an extremely unstable species with a lifetime of about 120 fs.⁷ The lifetime of 1,3-diphenyltrimethylene is more than 10^5 times longer ($\tau = 14\text{--}15$ ns)⁸ as a result of conjugative stabilization of the radical centers by phenyl substituents. Diradical intermediates **3a** and **3b** are also stabilized by conjugation with aromatic and/or carbonyl systems, and we might expect their lifetime to be on the nanosecond time scale. On the other hand, HPLC analysis of reaction mixtures of irradiation of dibenzonorcaradienes **1a–c** in neat methanol, 2-propanol, and in the presence of thiophenol did not detect dihydrophenanthrenes nor formaldehyde, acetone, or phenyl disul-

fide, respectively, the expected products of diradical **3** interception.

The thiophenol is one of the most efficient radical trapping agents, which reacts with benzyl radical at $k_{\text{RSH}} = 3.13 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.⁹ The absence of trapping products at 0.002 M concentration of thiophenol suggests that the lifetime of diradical **3** is shorter than 1 ms. The nanosecond laser photolysis¹⁰ of dibenzonorcaradienes **1a–c** allows one to observe an instant (on the time scale of the instruments) rise in absorbance as illustrated by the transient signal shown below in Figure 1.

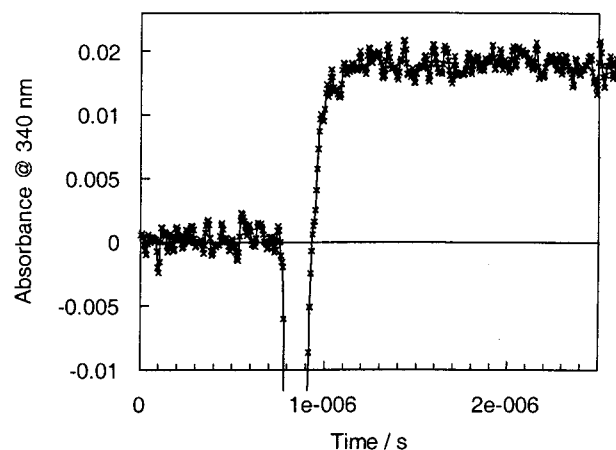


Figure 1. Laser (Nd:YAG) flash photolysis of *trans*-7-benzoyldibenzonorcaradiene (**1b**) in methanol at 355 nm.

This absorbance, which then stays constant for at least 2 ms, apparently corresponds to the product **2**,¹¹ which is

(6) Guziec, F. S.; Luzzio, F. A. *J. Org. Chem.* **1983**, *48*, 2434. Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7512.

(7) De Feyter, S.; Diau, E. W.-G.; Scala, A. A.; Zewail, A. H. *Chem. Phys. Lett.* **1999**, *303*, 249. Doubleday, C.; Bolton, K.; Peslherbe, G. H.; Hase, W. L. *J. Am. Chem. Soc.* **1996**, *118*, 9922.

(8) Karki, S. B.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Zona, T. A. *J. Am. Chem. Soc.* **1997**, *119*, 431.

(9) Wagner, P. J.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 287. Tronche, C.; Martinez, F. N.; Horner, J. H.; Newcomb, M. *Tetrahedron Lett.* **1996**, *37*, 5845. Newcomb, M.; Choi, S.-Y.; Horner, J. H. *J. Org. Chem.* **1999**, *64*, 1225.

(10) Time-resolve experiments were conducted using both Q-switched Nd:YAG (Serguievski, P.; Ford, W.E.; Rodgers, M. A. *J. Langmuir* **1996**, *12*, 348) and excimer (Andraos, J.; Chiang, Y.; Huang, G.-C.; Kresge, A. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 10605) laser systems.

formed within the duration of a laser pulse (~20 ns). These results combined with the literature data discussed above allow us to evaluate the lifetime of diradicals **3a,b** in the range between 1 and 20 ns.

The rotation around the central σ -bond in 1,3-diradicals, which leads to *cis*–*trans* isomerization of cyclopropanes, is a fast process for sterically unhindered systems, $k_{\text{rot}} \approx 10^{12} \text{ s}^{-1}$.^{7,12} We have conducted semiempirical calculations on diradical **3b** and found no significant steric barrier for rotation in that system.¹³ This result suggests that rotation in diradical **3b** can be considered virtually free. Conformational analysis of **3a**, on the other hand, predicts a substantial activation barrier ($\Delta H^\ddagger = 6.8$ – 7.4 kcal/mol) for such rotation, mainly due to steric interaction of the phenyl group (R' , Scheme 5) with the adjacent hydrogen. These results agree well with the lack of isomerization in photolysis of 7-methoxycarbonyl-7-phenyldibenzonorcaradiene (**1a**).

The diradical **3b** decays by three pathways: cyclization to *trans*- (**1b**) and *cis*- (**1c**) dibenzonorcaradienes and 1,2-hydrogen shift to form product **2b**, so $k_{\text{decay}} = k_{\text{trans}} + k_{\text{cis}} + k_{\text{H-shift}}$. Analysis of product distribution in low conversion photolyses of **1b** and **1c** provides an opportunity to determine relative rates of these processes. Thus, irradiation of **1b** at 300 nm for 60 s resulted in consumption of 8–10% of starting material and produced products **2b** and **1c** in the ratio of $\mathbf{1c}/\mathbf{2b} = 2.5 \pm 0.3$. The similar product ratio was observed in a single-flash photolysis using Xe-flash tubes (100 μs pulse duration),¹⁴ $\mathbf{1c}/\mathbf{2b} = 2.0 \pm 0.2$. This ratio represent the rate ratio of hydrogen shift versus *cis*-cyclization, $k_{\text{cis}}/k_{\text{H-shift}}$. (Scheme 5).

(11) UV spectra of starting materials and products can be found in the Supporting Information.

(12) Johnson, W. T. G.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1999**, *121*, 7766. Bergman, R. G.; Carter, W. L. *J. Am. Chem. Soc.* **1969**, *91*, 7411.

(13) Semiempirical calculation were performed using the Spartan Pro program (Wavefunction, Inc.) at the PM3 level.

(14) Xe-flash lamp system is described in Chiang, Y.; Hojatti, M.; Keeffe, J. R.; Kresge, A. J.; Schepp, N. P.; Wirz, J. *J. Am. Chem. Soc.* **1987**, *109*, 4000.

Photolysis of **1c** under identical conditions resulted in a different product ratio: $\mathbf{1b}/\mathbf{2b} = k_{\text{trans}}/k_{\text{H-shift}} = 8.4 \pm 0.6$.

Using the rate of hydrogen shift as a reference, we can conclude that cyclization of diradical intermediate **3b** to *trans*-7-benzoyldibenzonorcaradiene (**1b**) is four times faster than to the *cis*-isomer **1c**. The *trans*-isomer **1b** is 5 kcal/mol more stable than the *cis*-**1c** according to semiempirical calculations.¹³ We believe that this difference is mainly due to higher steric strain in the **1c**, as molecular mechanic (MMFF) calculations predict exactly the same energy difference between isomers. The slower rate of **1c** formation is apparently explained by the influence of the steric hindrance on the ring closure process.

Conclusion. Photolysis of dibenzonorcaradienes bearing an acyl or carbalkoxy substituent in the 7-position results in the cleavage of one of the cyclopropane bonds and formation of 1,3-diradicals. The major pathways of the decay of these diradicals are recombination with regeneration of cyclopropane ring and 1,2-hydrogen shift to form 9-substituted phenanthrenes. No carbene-derived products were detected in these reactions.

Apparently, electronic effects of carbonyl and phenyl groups are insufficient to make carbene formation fast enough to compete with formation of the 1,3-diradical. Substitution with heavy atoms, such chlorine or bromine, may be required to achieve photochemical α -carbonyl-carbene generation from 7-acyldibenzonorcaradienes.⁴

Acknowledgment. The authors thank Bowling Green State University for the financial support of this project.

Supporting Information Available: Procedures for preparation of compounds **1a,b** and photolysis of **1a–c**; ¹H, ¹³C, and mass spectra for compounds **1a–c** and **2a,b**; X-ray structure of **1b**. This material is available free of charge via the Internet at <http://www.acs.org>.

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