Pergamon

Tetrahedron Letters, Vol. 35, No. 30, pp. 5401-5404, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)01108-7

The Argon Laser-Jet Initiated, Multiple-Photon (Reluctant), Electrocyclic Ring Opening of 10,10-Diphenyl-9-(10*H*)-phenanthrenone : A Carbene and Biradical Modeling Study.

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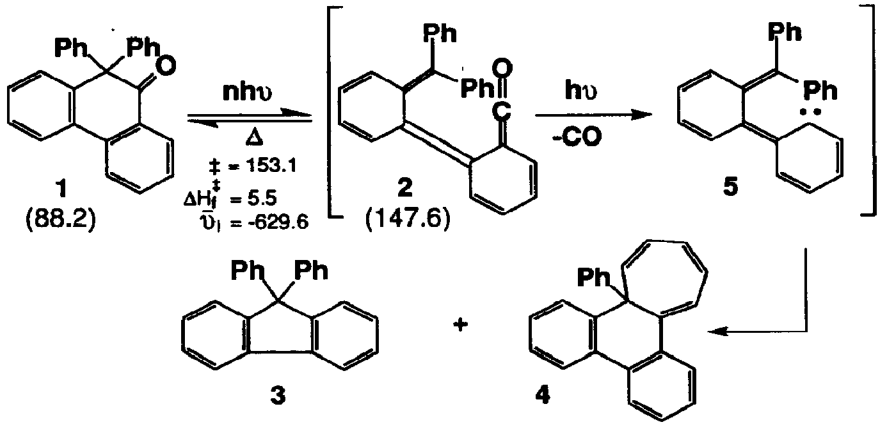
Abstract: While 10,10-diphenyl-9-(10*H*)-phenanthrenone (**1**) is inert under conventional irradiation conditions, it undergoes decarbonylation under high-intensity argon laser-jet conditions to form 9,9-diphenylfluorene (**3**) and the cycloheptatriene **4**. Molecular modeling studies indicate that **3** arises from collapse of the singlet carbene ^{1}**5** and the triene **4** from the triplet carbene ^{3}**5**.

Many potential photochemical reactions would seem to be highly favorable processes, and yet, are not observed. One such case involves the ketone **1** (Scheme 1).[1] The photochemical ring opening of **1** to the extended ketene methine **2** might be expected to be particularly facile via either a Norrish type I reaction or an electrocyclic ring opening. Contrary to expectations, low intensity irradiation of **1** (Rayonet Photochemical Reactor, 350 nm, 6 hours) led to virtually complete recovery of starting material. The intriguing possibility existed that this type of reluctant reaction might be accessible from a higher excited state, and that the argon laser-jet technique[2] might provide sufficiently high intensities to access these higher states through multiple-photon absorption. In fact, laser-jet irradiation of **1** (all UV lines 333.6-363.8 nm, 4 watts, 5 hours, benzene) does produce two new products: 9,9-diphenylfluorene



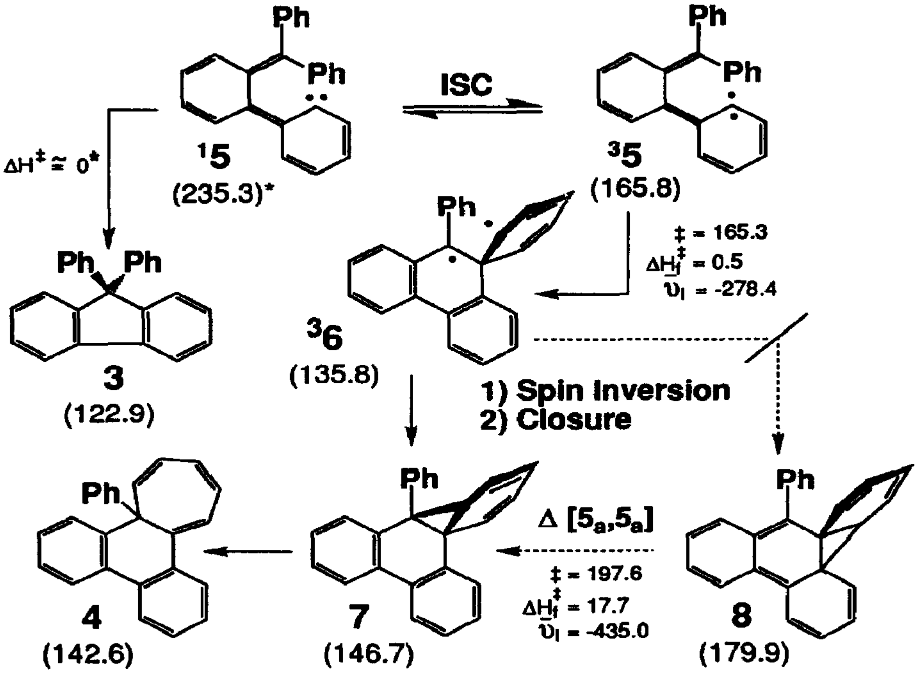
AM1 ΔH$_f$ values (kcal/mol) for minima and transition states are shown.
Scheme 1

(**3**) and the cycloheptatriene **4** (mp 150-152° C) in a ratio of about 15:85, respectively. The structure of **3** was confirmed by comparison with an authentic sample,[3] and that of **4** by x-ray crystallographic analysis.[4]

Both of these products are consistent with a mechanism involving a photochemical decarbonylation of the putative ketene **2** to form the carbene **5**. Attempts to trap either of these species with methanol in laser-jet reactions were unsuccessful. Apparently the ketene **2** is a very short-lived species as might be expected if it undergoes a facile cyclization back to **1**. Under these circumstances, the photochemical decarbonylation step would have to compete with the regeneration of the starting material **1**, and might only compete effectively at very high light intensities. This possibility is consistent with the small activation barrier calculated at the semiempirical AM1 level for the thermal cyclization of **2** to **1** (Scheme 1).[5]

Transient spectroscopic studies with **1** under a variety of conditions[6] revealed a single transient absorption at about 353 nm ($\tau = 3\ \mu s$) that was quenchable with molecular oxygen or isoprene. This absorption is consistent with intermediacy of a triplet π,π^* biphenyl excited state.[7] Furthermore, only a small amount of irreversible bleaching of this 353 nm transient was observed upon irradiation with a second dye laser pulse (420 nm) 2 μs after the initial excimer laser synthesis pulse at 308 nm. While these observations do not provide direct evidence for the intermediacy of either ketene **2** or carbene **5**, they do demonstrate that **2** is not formed in a conventional single-photon process, and can only be produced in a two-photon or higher order process which most likely involves excitation of the initially formed π,π^* biphenyl triplet.

This lack of definitive experimental evidence for the intermediacy of either **2** or **5** has led us to examine this system from a theoretical prospective with the following interesting results. Photochemical electrocyclic ring opening of **1** yields a highly twisted ketene **2**. This ketene might either undergo ring closure back to **1** or photochemical decarbonylation to the carbene **5**. Closs and coworkers have directly observed carbenes related to **5** at low temperatures, and found them to have triplet ground states.[8] Thus, while **5** would be expected to have a triplet ground state (^{3}**5**), it might be formed initially in its singlet state (^{1}**5**). Semiempirical MO calculations[5] indicate that no minimum for the singlet ^{1}**5** exists. Attempts to locate a minimum for ^{1}**5**, even with initial calculation of a numeric hessian, were unsuccessful; instead ^{1}**5** collapsed directly to 9,9-diphenylfluorene **3**, the minor product. The triplet carbene ^{3}**5** has a shallow minimum at a geometry similar to that of the ketene **2**, but this readily closes to a species that is best described as the triplet biradical ^{3}**6**. Consequently, according to this model, the carbenes ^{1}**5** and ^{3}**5** are probably only very short-lived transient species that collapse directly to **3** and biradical ^{3}**6**, respectively. These correlations are consistent with the aforementioned ratio of **3**:**4** which indicates that the triplet channel predominates. In principle, once formed ^{3}**6** could undergo spin inversion to ^{1}**6** which could be followed by collapse to either the bisnorcaradiene **7** or **8**. Calculations indicate that **7** is substantially lower in energy then **8** which has a highly disrupted aromatic system.[9] In accord with these expectations, two channels were found for collapse of ^{1}**6**; a local high energy channel accessed from geometries approximating that of **8** and collapsing directly to **8**, and a more global low energy channel accessed from all other geometries and collapsing directly to **7**. This overall process of intramolecular attack of a 2-alkylidenylcyclohexadienylidene on a pendent phenyl group to form a norcaradiene has precedent in the work of Bernard and Shechter.[10] In the present case, the bisnorcaradienes **7** and **8** constitute a set related to one another via a symmetry allowed [$5_a,5_a$] sigmatropic shift.[11] Estimation of the transition state for this reaction indicates that it more closely resembles **8**. Since spin inversion of ^{3}**6** injects ^{1}**6** at the approximate midpoint of the [$5_a,5_a$] hypersurface, ^{1}**6** should collapse to **7** exclusively. Indeed, singlet geometry reoptimization at the optimized geometry of the triplet diradical ^{3}**6** leads directly to **7** and not to **8**. This calculated pathway by-passes the high energy bisnorcaradiene isomer **8** which might otherwise have been invoked as a pivotal intermediate in any a priori mechanism for the formation of the cycloheptatriene **4** from the singlet carbene ^{1}**5**.



* No minimum could be found for ^{1}5. The energy shown is for a structure similar to ketene 2.

Scheme 2

These results provide an excellent example of the correlation between reaction modeling and complex mechanisms in carbene and biradical chemistry. In addition, they further demonstrate that the argon laser-jet technique is sufficiently powerful to generate isolable quantities of high intensity multiple-photon products at least at the three-photon level.

Acknowledgments. We thank the National Science Foundation for financial support of this work (CHE-8914889 and CHE-9122141). Also we would like to thank Professor Matthew S. Platz of The Ohio State University for making his transient spectroscopy instrumentation available to us, and

Professor Linda J. Johnston of the National Research Council of Canada for conducting the transient spectroscopic experiments reported in this work.

REFERENCES AND NOTES

1. Empis, J. M. A.; Franco, Mª. L. T. M. B.; Herold, B. J. ; Queiroga, J. J. R. P. *Tetrahedron Lett.* **1975**, 4153. Schlenk, W.; Bergmann, E. *Liebig's Ann. Chem.* **1928**, *463*, 209.
2. Wilson, R. M.; Hannemann, K.; Schnapp, K. A.; Memarian, H. R.; Azadnia, A. *SPSE Proc. Summer Symp. Photochem. Imaging,* **1988**, 167. Wilson, R. M.; Schnapp, K. A.; Hannemann, K.; Ho, D. M.; Memarian, H. R.; Azadnia, A.; Pinhas, A. R.; Figley, T. M. *Spectrochim. Acta,* **1990**, *46A*, 551. Wilson, R. M.; Adam, W.; Schulte Oestrich, R. *The Spectrum* **1991**, *4*, Fall Issue, 8. Wilson, R. M.; Schnapp, K. A. *Chem. Rev.* **1993**, *93*, 223.
3. Lagu, A.; Mark, Jr., H. B. *J. Org. Chem.* **1977**, *42*, 1063.
4. The x-ray structure of **1** was determined from a single monoclinic crystal $P2_1/c$ of unit cell dimensions: a = 12.631(4) Å, b = 8.839(2) Å, c = 16.766(4) Å, β = 103.59(2)°, V=1819.4(9) Å^3, Z= 4, T = 21° C, Mo Kα radiation, Siemens, R3m/V diffractometer. The structure was solved from 1169 observed reflections ($F > 4.0\sigma(F)$) using direct methods in SHELXTL PLUS and full-matrix least-squares to obtain a final R = 7.58 %, wR = 8.48 % and a goodness-of-fit of 1.27. The X-ray structure of **4** was determined from a single monoclinic crystal $P2_1/c$) of unit cell dimensions: a = 7.663(8) Å, b = 21.353(13) Å, c = 10.374 (4) Å, β = 96.40(6)°, V=1687(2) Å^3, Z= 4, T = 23° C, Mo Kα radiation, Siemens, R3m/V diffractometer. The structure was solved from 1870 observed reflections ($F > 4.0\sigma(F)$) using direct methods in SHELXTL PLUS and full-matrix least-squares to obtain a final R = 5.51 %, wR = 5.49 % and a goodness-of-fit of 1.35. The X-ray crystal structure of the parent molecule related to **4** (-Ph replaced by -H) has been determined, ref. 11b.
5. Calculations were conducted using Hyperchem, Version 2 and Spartan, Versions 2.1 and 3.0, on a Silicon Graphics Indigo XS24 4000. Minimizations, molecular dynamics and energy calculations were conducted using AM1, UHF or RHF, to gradients of <0.05 kcal/(Å-mol).
6. Transient spectroscopic studies were conducted with an XeCl excimer laser at 308 nm (Lambda Physik or Lumonics, EX-530) in CH_2Cl_2, PhH or CH_3CN as solvent. Absorption spectra were monitored with either a 1000 watt xenon arc and an optical multichannel analyzer or a 150 watt lamp and a photomultiplier . In the two-laser experiments, the second laser was a Lumonics HD-500 dye laser (Stilbene 420 dye, 355 nm pumping from a Nd:YAG laser).
7. Guérin, B.; Johnston, L. J.; Quach, T. *J. Org. Chem.* **1988**, *53*, 2826.
8. Closs, G. L.; Kaplan, L. R.; Bendall, V. I. *J. Am. Chem. Soc.* **1967**, *89*, 3376.
9. At this level, UHF tends to overestimate the stabilities of triplets and biradicals, and so comparison of singlet and triplet energies is not reliable.
10. Bernard, R. E.; Shechter, H. *Tetrahedron Lett.* **1972**, 4529.
11. Dürr, H.; Pauly, K.-H.; Scheidhauer, P.; Fischer, K. *J. Chem. Res.* **1989**, 242. Dürr, H.; Pauly, K.-H.; Fischer, K. *Chem. Ber.* **1983**, *116*, 2855. Parker, R. H.; Jones, W. M. *J. Org. Chem.* **1978**, *43*, 2548. Pauly, K.-H.; Dürr, H. *Tetrahedron Lett.* **1976**, 3649. Vedejs, E.; Wilber, W. R. *Tetrahedron Lett.* **1975**, 2679. Dürr, H.; Kausch, M.; Kober, H. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 670. Mitsuhashi, T.; Jones, W. M. *J. Chem. Soc., Chem. Commun.* **1974**, 103. Gruber, G. W.; Pomerantz, M. *Tetrahedron Lett.* **1970**, 3755.

(*Received in USA* 21 *March* 1994; *revised* 1 *June* 1994; *accepted* 7 *June* 1994)