



S0040-4039(96)00284-5

Sequential Multiple-Photon Photochemistry of Sterically Congested Enones

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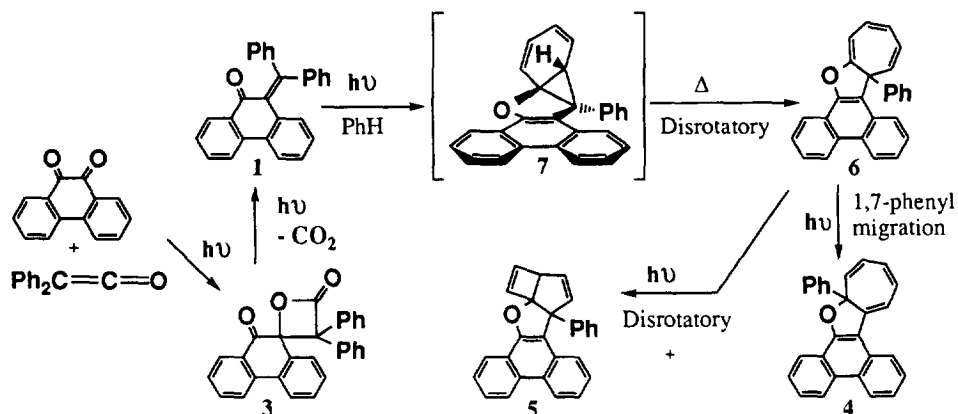
Abstract: The photochemistry of sterically hindered enones **1** and **2** is described. A novel photorearrangement occurs in both systems which involves carbonyl attack on the adjacent phenyl ring, expansion of that ring to a cycloheptatriene and subsequent photochemically induced 1,7-phenyl migration. Copyright © 1996 Elsevier Science Ltd

The photochemistry of enones has received a great deal of attention over the past twenty years.¹ Most studies have dealt with the mechanistically interesting reactions of cyclic enones. Acyclic enones, in contrast, tend to exhibit less complex photochemistry, since they can dissipate the energy of excitation via cis-trans isomerization about the carbon-carbon double bond. We have examined the photochemistry of the acyclic enones **1** and **2** (Schemes 1 and 2, respectively) and observed a unique photorearrangement which probably is facilitated by the extreme steric congestion in these molecules.

Enone **1** is prepared through the photochemical addition of phenanthrenequinone to diphenylketene which produces spirolactone **3** (Scheme 1).² Subsequent photodecarboxylation of **3** produces **1**.³ Although the carbon-carbon double bond of enone **1** is acyclic, this system has been constrained in an *s*-cis conformation with a high degree of steric congestion between the cis β -phenyl group and the carbonyl oxygen. Based upon x-ray crystal data and semi-empirical calculations,⁴ the distance between the carbonyl oxygen and the ipso position of the cis β -phenyl group is only 3.02 Å (x-ray) or 3.09 Å (calculations). When enone **1** is irradiated in benzene with low intensity UV light (350 nm), two photoproducts are formed: triene **4** (32%) and cyclobutene **5** (9%). High-intensity argon ion laser-jet irradiation (333, 351 and 364 nm lines)⁵ of **1** in benzene afforded the new photoproduct **6** in addition to **4** and **5**. Further studies confirmed that when **6** is irradiated under low-intensity conditions, it undergoes a very facile 1,7-phenyl migration to form **4** and a somewhat less favorable, electrocyclic ring closure to form the cyclobutene **5**. In contrast, **4** is stable under both low- and high-intensity conditions with no reverse 1,7-phenyl migration to form **6** being detected. These observations are consistent with calculations⁴ which indicate that the ground state of **4** is about 2.1 kcal/mol lower in energy than that of **6**, and that the vertical excited singlet state of **4** is about 13 kcal/mol lower.

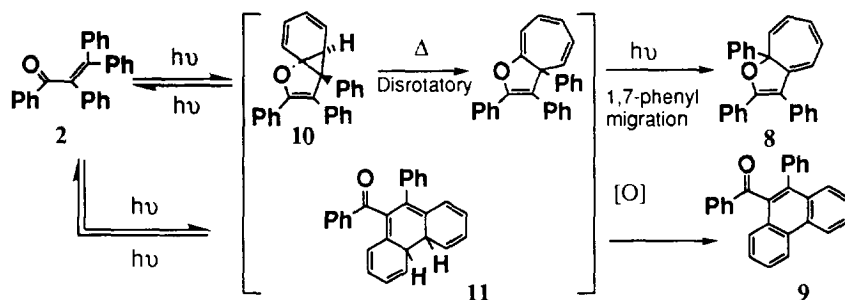
The exclusive formation of **6** under high-intensity conditions was rather puzzling at first. Since the formation of **6** appears to require only a single photon, its formation would not be expected to be favored by high-intensity (multiple-photon) conditions. This apparent inconsistency is readily understood in terms of the mode of irradiation in the argon laser-jet apparatus. The primary

photoproduct of this reaction is expected to be the norcaradiene **7** which either does not absorb strongly at the laser lines or is photochemically inert.⁷ Furthermore, if the lifetime of **7** significantly exceeds its residence time in the laser focal region (ca. 10 μ s), then cycloheptatriene **6** would be formed in the dark after passing through the focal region of the laser, and would survive to be isolated.



Scheme 1

In an effort to see whether the *s-cis* constraint and steric congestion present in enone **1** play a role in this photoreaction, the enone **2**⁸ was also studied (Scheme 2). Enone **2** has much less restricted rotation about the formal single bond between the carbonyl and olefin moieties. The low-intensity photochemistry of enone **2** produced two photoproducts, triene **8** (12%), and the phenanthrene **9** (35%). High-intensity laser-jet irradiation of **2** strongly suppress the formation of both **8** and **9** in a variety of solvents including C₆H₆ and CH₃CN. Apparently secondary absorption by the intermediates **10** and the dihydrophenanthrene **11** leads to their efficient return to starting material under these conditions.⁹ Nevertheless, the mechanism for the formation of triene **8** seems to be analogous to that of triene **4** and is outlined in Scheme 2. We have examined other sterically congested and constrained enones, including β -phenylchalcone, but to date only the two enones reported here have been found to undergo this photorearrangement.



Scheme 2

Both of the photoreactive enones **1** and **2** afford detectable transient intermediates in LFP (laser flash photolysis) experiments. Enone **1** gives rise to a transient with $\lambda_{\max} = 320$ and 450 nm ($\tau = 6.7$ μ s, N_2). Enone **2** affords a similar transient with $\lambda_{\max} = 300$ and 425 nm ($\tau = 12$ μ s, N_2).¹⁰ Molecular oxygen, azide ion, methanol, cyclooctadiene, fumaronitrile, sulfuric acid and TFA/methanol do not substantially quench the formation of either of these transient species nor affect their lifetimes within the time frame of the experiments (ca. 30 μ s). These observations exclude the possibility that these transients arise from the starting ketone triplet excited states or triplet biradical precursors to the norcaradienes **7** and **10**.⁷ The long wavelength absorption maxima also exclude the possibility that the transients are due to the norcaradienes **7** and **10**, but are consistent with their assignment to dihydrophenanthrenes.^{10,11} Thus, it may be that the observed transient spectra are dominated by the more strongly absorbing dihydrophenanthrene intermediates and may not be due to species involved in the formation of **6** and **8**. Further efforts to obtain information about the intermediates involved in the reaction of **1** to **4** will be reported in a subsequent paper.⁷

In summary, a new photoreaction of phenyl enones has been observed which involves initial attack of the carbonyl oxygen at the ipso position of a neighboring aromatic ring followed by ring expansion to a cycloheptatriene system. In addition, the reaction of **1** also constitutes an unusual example of the use of the high-intensity laser-jet technique to detect primary photoproducts which might otherwise go unobserved as a result of subsequent photochemistry under more conventional continuous irradiation conditions.

Acknowledgments: We thank Professor Sheldon G. Shore of The Ohio State University for providing us with access to his low-temperature x-ray facilities. KAS thanks the Kentucky NSF/EPSCoR (1993-REG-35, 1994-REG-46) and Research Corporation (RE Award C-3466) for financial support of this work. RMW thanks the NSF (CHE-9122141) for financial support. CB thanks NSERC for financial support.

References and Notes:

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- Similar transformations have been reported by Terpetschnig, E.; Penn, G.; Kollenz, G.; Peters, K.; Peters, E. M. *Tetrahedron*, **1991**, *47*, 3045.
- The structures of all new compounds were consistent with spectroscopic data; the structures of the photoproducts (**1**, **4-6** and **9**) have been determined by single crystal x-ray analysis. The following characteristic data was observed: **1**: mp 140-142°C; IR (CH₂Cl₂) 1672 cm⁻¹; HRMS, *m/e* (M⁺) calcd for C₂₇H₁₈O 358.1358, found 358.1372; a single monoclinic crystal P2₁/n of cell dimensions: a = 8.672(2) Å, b = 8.688(2) Å, c = 24.722(5) Å, $\beta = 93.08(3)^\circ$, V = 1859.9(7) Å³, Z = 4, T = -40°C, Enraf Nonius CAD-4 diffractometer. The structure was solved from 2343 (F>3.0 σ (F)) observed reflections using direct methods in SHELXTL PLUS, the difference Fourier technique and full-matrix least squares to obtain a final R = 5.82%, wR = 6.04% and a goodness-of-fit of 1.32. **3**: mp 231- 232°C; IR (CH₂Cl₂) 1825, 1701 cm⁻¹; HRMS *m/e* (M⁺) calcd for C₂₈H₁₈O₃ 402.1256, found 402.1307. **4**: yellow needles, mp 177-179°C; ¹H NMR (300 MHz, CDCl₃) δ 6.27 (m, 2H), 6.49 (dd, *J* = 6.5, 10.3 Hz, 1H), 6.61 (dd, *J* = 6.9, 11.0 Hz, 1H), 7.21 (m, 3H), 7.42 (m, 3H), 7.58 (m, 2H), 7.68 (m, 2H), 8.20 (d, *J* = 7.7 Hz, 1H), 8.49 (d, *J* = 8.0 Hz, 1H), 8.65 (dd, *J* = 8.2, 16.2 Hz, 2H); HRMS *m/e* (M⁺) calcd for C₂₇H₁₈O 358.1358, found 358.1333; a single triclinic crystal P₁ of unit cell dimensions: a = 9.217(3) Å, b = 9.949(3) Å, c = 10.973(3) Å, $\alpha = 79.92(2)^\circ$, $\beta = 74.16(3)^\circ$, $\gamma =$

- 73.99(2)°, $V = 925.1(5)\text{\AA}^3$, $Z = 2$, $T = 24^\circ\text{C}$, 2059 observed reflections ($F > 3.0\sigma(F)$), Siemens, R3m/V diffractometer, solved as in above to obtain a final $R = 6.80\%$, $wR = 6.30\%$ and a goodness-of-fit of 1.28. **5**: pale yellow blocks, mp 198-200°C; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 5.73 (d, $J = 2.2$ Hz, 1H), 6.23 (dd, $J = 1.9, 5.9$ Hz, 1H), 6.63 (d, $J = 2.2$ Hz, 1H), 6.76 (d, $J = 6.0$ Hz, 1H) 7.22 (m, 6H), 7.43 (m, 3H), 7.70 (m, 2H), 8.24 (d, $J = 7.2$ Hz, 1H), 8.70 (dd, $J = 8.3, 15.7$ Hz, 2H); HRMS m/e (M^+) calcd for $\text{C}_{27}\text{H}_{18}\text{O}$ 358.1358, found 358.1402; a single orthorhombic crystal $\text{P}2_12_12_1$ of unit cell dimensions: $a = 9.442(2)\text{\AA}$, $b = 10.733(2)\text{\AA}$, $c = 18.333(7)\text{\AA}$, $V = 1857.9(7)\text{\AA}^3$, $Z = 4$, $T = 25^\circ\text{C}$, 1981 observed reflections ($F > 3.0\sigma(F)$), diffractometer and solution as for **4** to obtain a final $R = 4.13\%$, $wR = 5.06\%$ and a goodness-of-fit of 1.25. **6**: colorless crystals, mp 167-169°C; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 6.34 (m, 2H), 6.55 (dd, $J = 6.4, 10.5$ Hz, 1H), 6.72 (dd, $J = 6.8, 11.1$ Hz, 1H), 7.29 (m, 3H), 7.41 (m, 3H), 7.53 (m, 2H), 7.67 (m, 2H), 8.22 (d, $J = 7.5$ Hz, 1H), 8.53 (d, $J = 8.1$ Hz, 1H), 8.68 (dd, $J = 8.5, 17.1$ Hz, 2H); HRMS m/e (M^+) calcd for $\text{C}_{27}\text{H}_{18}\text{O}$ 358.1358, found 358.1386; a single monoclinic crystal $\text{P}2_1/n$ of unit cell dimensions: $a = 14.249(3)\text{\AA}$, $b = 8.5350(10)\text{\AA}$, $c = 15.568(3)\text{\AA}$, $\beta = 101.110(10)^\circ$, $V = 1857.8(5)\text{\AA}^3$, $Z = 4$, $T = 25^\circ\text{C}$, 1274 observed reflections ($F > 3.0\sigma(F)$), diffractometer and solution as for **4** to obtain a final $R = 6.82\%$, $wR = 6.58\%$ and a goodness-of-fit of 1.27. **8**: mp 85-86°C; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 6.18 (m, 3H), 6.39 (m, 2H), 7.23 (m, 6H), 7.42 (m, 9H); HRMS m/e (M^+) calcd for $\text{C}_{27}\text{H}_{20}\text{O}$ 360.1514, found 360.1546. **9**: colorless crystals, mp 171-174°C; IR (CH_2Cl_2) 1685 cm^{-1} ; HRMS m/e (M^+) calcd for $\text{C}_{27}\text{H}_{18}\text{O}$ 358.1358, found 358.1372; a single monoclinic crystal $\text{P}2_1/n$ of unit cell dimensions: $a = 10.022(3)\text{\AA}$, $b = 13.008(2)\text{\AA}$, $c = 14.531(3)\text{\AA}$, $\beta = 99.07(2)^\circ$, $V = 1870.7(7)\text{\AA}^3$, $Z = 4$, $T = 25^\circ\text{C}$, 2287 observed reflections ($F > 3.0\sigma(F)$), diffractometer and solution as for **4** to obtain a final $R = 5.79\%$, $wR = 5.98\%$ and a goodness of fit of 1.39.
- Calculations were conducted using Hyperchem, release 2, on a Silicon Graphics Indigo XS24 4000. Minimizations and energy calculations were conducted using AM1, UHF or RHF, to gradients of < 0.03 kcal/(\AA -mol).
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 - While there is no direct evidence for the stereochemistry of **7**, the stereochemistry shown in Scheme 1 is that of the lowest energy isomer, and perhaps of significance, also that expected from a photochemically allowed [$4_s + 2_a$] photocycloaddition.
 - For further mechanistic studies of the photoreactions of enone **1**, see: Schnapp, K. A.; Motz, P. L.; Wilson R. M.; Winter, D.; Krause Bauer, J. A. *Tetrahedron Lett.* submitted for publication.
 - Enone **2** was prepared using a modification of the procedure of House (House, H. O.; Reif, D. *J. J. Am. Chem. Soc.* **1955**, *77*, 6525) to produce the alcohol which was subsequently oxidized with PCC to produce the enone.
 - Muszkat, K. A.; Fischer, E. *J. Chem. Soc. B* **1967**, 662. Repinec, S. T.; Sension, R. J.; Szarka, A. Z.; Hochstrasser, R. M. *J. Phys. Chem.* **1991**, *95*, 10380.
 - In laser flash photolysis studies, the samples were excited with either an excimer laser at 308 nm (Lumonics EX-510) or with a YAG laser at 266 nm (Spectra Physics GCR 12) in acetonitrile. The analyzing beam consisted of a pulsed 150W Xe lamp and light intensities were detected by a photomultiplier/monochromator system. Signals were captured on a Tektronix TDS 520 digital scope. The experimental set-up was integrated to a MacIntosh IICi and the programs for data acquisition and analysis were written in Labview 2.2. A flow system was employed to insure that for each laser pulse a fresh sample was irradiated. Similar spectra were obtained in benzene with 308 nm excitation.
 - While no phenanthrene cyclization was observed when **1** was irradiated in benzene, the phenanthrene corresponding to **9** was isolated when **1** was irradiated in methanol, see ref. 7.