Photoaddition of Alkenes to Conjugated α-Diketones: Tandem Cyclizations Leading to Tetrasubstituted Furans[1a]

Ashis K. Mukherjee, Paul Margaretha,[1b] and William C. Agosta*

*The Laboratories of The Rockefeller University, New York, New York 10021-6399*

Photocycloaddition of **9a**−**c** with **2** leads cleanly to tetrasubstituted furans **12a**−**c**, respectively, in yields of ~85%. The reactive triplet is efficiently sensitized by 2-benzoylnaphthalene and quenched by anthracene, indicating that E_T is in the range 43−58 kcal/mol. A mechanism is proposed involving an alkyl propargyl biradical (as **10**) that closes first to a vinyl carbene (as **11**) and then to product. Reaction of **9c** with **20** furnishes only **22**, and this result rules out an alternative mechanism in which the order of steps leading to the carbene is reversed.

Photocycloaddition of simple alkenes to various 2-alkynylcycloalkenones leads to tricyclic furans in a process that we have explained as shown in the reaction of **1** with tetramethylethylene (**2**). Thus, biradical **3**, formed on

1   2   3   4   5

6   7   8
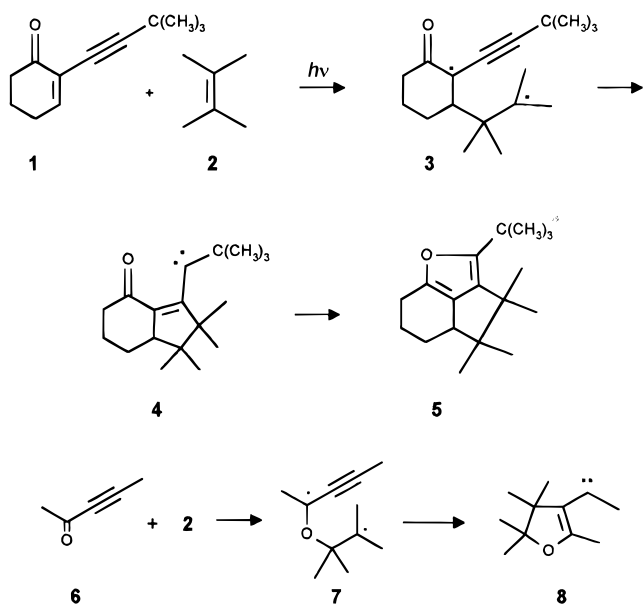
addition of **2** to triplet **1**, closes on the triple bond to yield β-acyl α,β-unsaturated carbene **4**. This carbene then undergoes electrocyclic closure on the carbonyl group to give the observed furan **5**.[2] The acyl group in **4** serves as an efficient carbene trap, and the gas chromatographic yields of furans such as **5** are ~90%. This cycloaddition is related to the previously described[3,4] photochemical addition of alkenes to simple conjugated alkynones to yield products derived from carbenes (see **6** + **2** → **7** → **8**).

Our experience with these two related reactions suggested investigation of photochemical addition of alkenes to conjugated acetylenic α-diketones. This reaction might proceed as suggested for **9a** and **2**, although we were
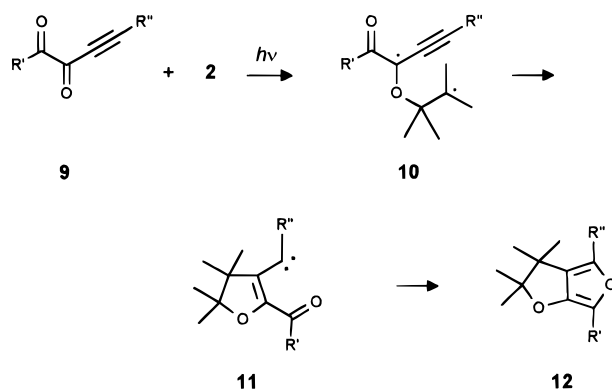
aware that the excited states and photochemistry of α-diketones differ considerably from those of simple carbonyl compounds.[5] We have now investigated this question and report that the photochemical reaction between **9a** and **2** proceeds to form **12a**, as shown. Our results with this and several other successful examples of this new process are described below. Preparative reactions are given first, followed by photochemical experiments.

9   10   11   12

a, R' = R" = CH₃; **b,** R' = C₆H₅, R" = CH₃; **c,** R' = CH₃, R" = C₆H₅

Preparative Reactions. The only previous example known to us of an acetylenic α-diketone was prepared by Steglich in the course of developing a flexible sequence for the synthesis of α-diketones.[6] We found this method to be satisfactory for the synthesis of **9a**−**c**, the three ketones we have used here. As shown for the synthesis of **9a**, alanine (**13**) was first converted to **14** on condensation with warm trifluoroacetic anhydride. The acidic center of **14** was then blocked by base-catalyzed Michael reaction with *tert*-butyl acrylate. Product **15** was treated with propynyllithium, and the resulting adduct **16** was then hydrolyzed to **9a** in 90% formic acid. For α-diketone **9b**, alanine (**13**) was replaced by phenylglycine (**17**), and for **9c**, alanine was used with phenylacetylene (**18**) in place of propyne. Ketones **9a**−**c** were purified by spinning-disk chromatography before irradiation.

Photochemical Results. Ketones **9a**−**c** were irradiated (λ > 340 nm) in benzene solution containing ~10 equiv of tetramethylethylene (**2**). The ketones reacted

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1996.
(1) (a) A portion of this work has appeared as a preliminary communication: Mukherjee, A. K.; Agosta, W. C. *J. Chem. Soc., Chem. Commun.* **1994**, 1821. (b) Institut für Organische Chemie, Universität Hamburg.
(2) Margaretha, P.; Reichow, S.; Agosta, W. C. *J. Chem. Soc., Chem. Commun.* **1992**, 797; *J. Org. Chem.* **1994**, *59*, 5393.
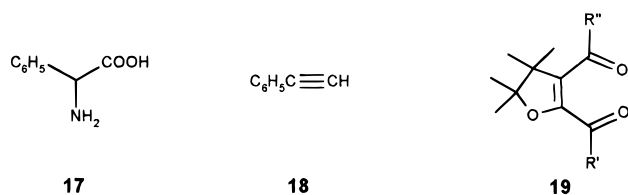(3) Hussain, S.; Agosta, W. C. *Tetrahedron* **1981**, *37*, 3301.
(4) Saba, S.; Wolff, S.; Schröder, C.; Margaretha, P.; Agosta, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 6902.

(5) Rubin, M. B. *Top. Curr. Chem.* **1985**, *129*, 1; **1969**, *13*, 251. Monroe, B. M. *Adv. Photochem.* **1971**, *8*, 77.
(6) Leyendecker, J.; Niewöhner, U.; Steglich, W. *Tetrahedron Lett.* **1983**, *24*, 2375 and references cited therein.
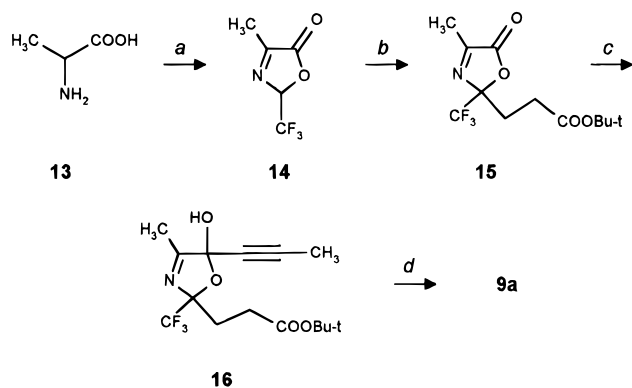
a, (CF₃CO)₂O, Δ; b, CH₂=CHCOOBu-t, EtN₃; c, CH₃C≡CH, BuLi; d, 90% HCOOH

a, R' = R" = CH₃; **b**, R' = C₆H₅, R" = CH₃; **c**, R' = CH₃, R" = C₆H₅

rapidly under these conditions, and within 2.5 h each was completely destroyed. Gas chromatographic analysis showed essentially a single product in each case. These products were isolated in yields of ~85% by spinning disk chromatography, and structures **12a**−**c**, respectively, could be assigned to them on the basis of their spectroscopic properties. These properties indicated that each was a 1:1 adduct between the appropriate ketone and **2**, that each lacked a carbonyl group, and that each had four signals in its ^{13}C NMR spectrum typical of a furan ring. In **12a**, for example, these signals appeared at δ 145.50, 137.74, 126.04, and 122.95. As expected for such poly-alkylated furans, these compounds were very susceptible to air oxidation. For **12a,c** we carried out this oxidation under controlled conditions by stirring a solution of each furan in benzene containing silica gel in the air for 24 h. This oxidation led to the much more stable α,β-unsaturated α-diketones **19a,c** in a reaction that provides independent support for the structures assigned to **12a**−**c**.

Ketone **9c** undergoes similar addition to isobutylene (**20**). Spectroscopic data indicate the sole product to be **22**, which is the adduct resulting from biradical intermediate **21**. This is the expected, more stable of the two possible biradicals from addition of **20** to **9c**. Such behavior is in keeping with previous observations in related reactions, where the products from addition of **20** and other 1,1-disubstituted ethylenes always arise from the more stable biradical.[2,7,8] It is worth noting that this result excludes an alternative mode of addition of **20** to **9c** that had to be considered owing to the following earlier observations. It has long been known that 4-phenyl-3-butyn-2-one (**23**) reacts with alkenes only at the triple bond. Reaction between **23** and **2**, for example,
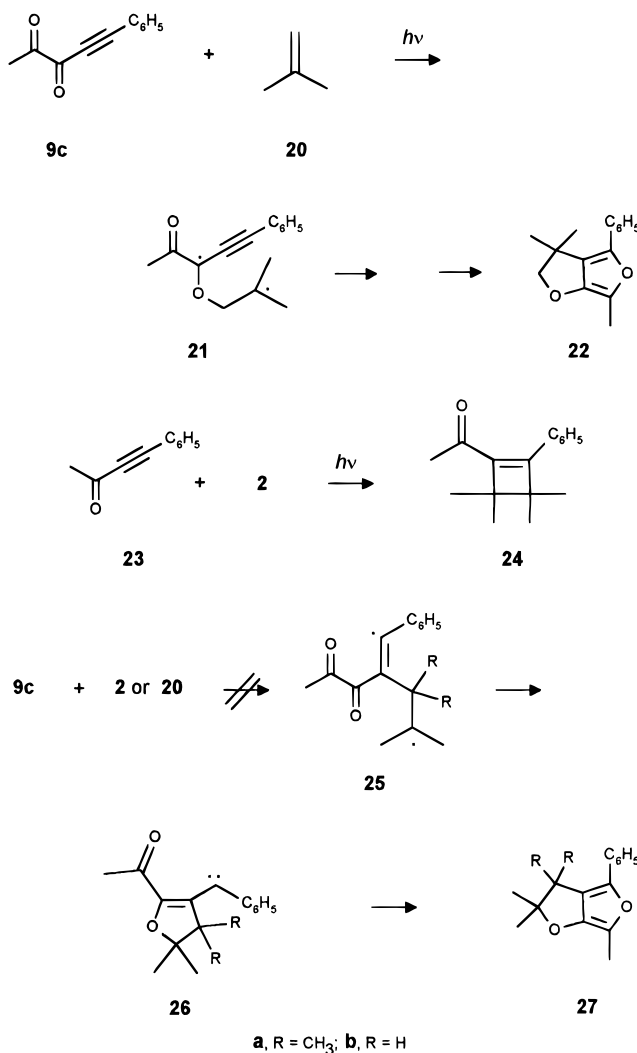
yields cyclobutene **24** as the only product.[9] This is in contrast to the behavior of **6** and other simple conjugated acetylenic ketones that yield oxetanes and furan derivatives but not cyclobutenes.[3,4] If phenyl-substitution in **9c** had an effect on the ynedione chromophore similar to its effect on **23**, reaction of **9c** with **2** and **20** could proceed through initial alkene addition to the triple bond, leading to biradicals **25a** and **25b**, respectively. These biradicals could then close to carbenes **26a,b**. The final product from **2** would still be the observed adduct **27a** (≡ **12c**), but from **20** this mode of addition would lead to **27b** rather than the observed adduct **22**. The failure of this reaction to yield either **27b** or a cyclobutene adduct is evidence that phenyl substitution on the triple bond does not influence the qualitative photochemical behavior of these acetylenic α-diketones.

We have also investigated the excited state responsible for these reactions through quenching and sensitization experiments. The reaction between **9a** and **2** was efficiently sensitized by 2-benzoylnaphthalene (E_T 59.1 kcal/mol[10]) and quenched by anthracene (E$_T$ 42 kcal/mol[10]) on irradiation (λ > 400 nm) in benzene.[11] Naphthalene did not quench the reaction. These findings point to an active triplet state with E_T in the range 43−58 kcal/mol. For comparison, E_T for the reactive triplets of

(7) Rathjen, H.-J.; Margaretha, P.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1991**, *113*, 3904.

(8) Margaretha, P.; Rathjen, H.-J.; Agosta, W. C. *Tetrahedron Lett.* **1990**, *31*, 3245.

(9) Fujita, K.; Yamamoto, K.; Shono, T. *Nippon Kagaku Kaishu* **1974**, 86.

(10) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker, Inc.: New York, 1973; pp 3−5.

biacetyl and **6** are 56[12] and ∼73−74 kcal/mol,[13] respectively. From its energy, the reactive triplet of **9a** thus appears to be a modified α-diketone triplet. We also found that **9a**(S$_1$) could not be captured as an oxetane (or any other singlet derived product) in the presence of high concentrations of alkene, although **6**(S$_1$) can be captured in this manner.[4] From **9a**, at low or high concentrations of **2** the only product obtained was **12a**.

These experiments demonstrate that alkene addition to these triplet ynediones provides an efficient route to highly substituted furofurans. They also provide the first information concerning the chemical and physical properties of the conjugated acetylenic α-diketone chromophore. In the reported reactions, the ynediones add alkenes like a simple conjugated acetylenic ketone, although the energy of the reactive triplet is more similar to that of a simple α-diketone.

Experimental Section

Materials and General Procedures. Preparative gas chromatography (GC) was carried out on a Varian Aerograph Model 920 gas chromatograph with a SE-30, 10-ft column on Chromosorb-W, packed in 0.25-in. aluminum tubing. Analytical GLC was carried out isothermally using internal standards on an HP-5890 temperature programmable gas chromatograph using an Alltech Econo-Cap (30 m × 0.25 mm) capillary column with a film thickness of 0.25 mm. All NMR spectra were recorded on a GE Model QE-300 (300 MHz for protons) spectrometer and are reported in parts per million downfield from tetramethylsilane (δ). Melting points were determined by using a Thomas-Hoover capillary melting point apparatus. Infrared spectra were recorded on a Perkin-Elmer Model 237B grating spectrophotometer or on a Perkin-Elmer 1870 Fourier-transform spectrophotometer, either neat or in KBr pellets. Ultraviolet absorption spectra were recorded on a Cary Model 14 recording instrument. All spinning disk chromatographic separations were carried out on a Chromatotron (Harrison Model 7924 T) using silica gel-coated (2- or 4-mm thick) glass rotors. Unless otherwise noted, photochemical reactions were carried out using a Hanovia 450-W medium-pressure mercury lamp in a Pyrex-jacketed immersion well with a uranium-glass filter (λ > 340 nm). All solutions were outgassed by passing nitrogen through them and were irradiated in toroidal Pyrex vessels under a nitrogen atmosphere unless otherwise mentioned. Benzene was used as solvent for all of the UV measurements.

4-Methyl-2-(trifluoromethyl)-5(2H)-oxazolone (14) and 4-Phenyl-2-(trifluoromethyl)-5(2H)-oxazolone[14] (28). These were prepared from the respective amino acid by the route previously employed by Steglich and co-workers[6] in good to moderate yields. For **14**, a solution of 3.0 g of alanine (or for **28**, 4.0 g of phenylglycine) in 12.0 mL of trifluoroacetic anhydride was heated at reflux in a 100 mL flask for 2.5 h. Analytical gas chromatography was used to monitor the reaction. Excesses of trifluoroacetic anhydride and trifluoroacetic acid formed in the reaction were removed by distillation. Spinning-disk chromatography was used to purify the product. For **14**: ¹H NMR (CDCl$_3$) δ 6.20−6.15 (m, 1 H), 2.42 (m, 3 H); ¹³C NMR (CDCl$_3$) δ 166.6, 164.0, 125.7, 122.0, 118.2, 116.4, 114.5, 13.8. For **28**: mp 85−86 °C; ¹H NMR (CDCl$_3$) δ 8.43−8.38 (m, 2 H), 7.67−7.63 (m, 1 H), 7.56−7.50 (m, 2 H), 6.30−6.25 (m, 1 H); ¹³C NMR (CDCl$_3$) δ 163.0, 160.7, 134.1, 129.12,

129.08, 127.1, 122.2, 118.5, 92.5 (q); HRMS *m/z* 229.0358 (M$^+$), calcd for C$_{10}$H$_6$F$_3$NO$_2$ 229.0350. The spectroscopic properties of both **14** and **28** are in agreement with those previously reported for these compounds.[15]

***tert*-Butyl 2-(4-Methyl-5-oxo-2-(trifluoromethyl)-2H-oxazolyl)propionate (15) and *tert*-Butyl 2-(4-Phenyl-5-oxo-(trifluoromethyl)-2H-oxazolyl)propionate[14] (29).** These compounds were prepared following the method of Steglich.[6] A solution of 1.29 g (0.0129 M) of triethylamine in 20 mL of CH$_2$Cl$_2$ was added to a stirred solution of **14** or **28** (0.0129 M) containing 1.66 g of *tert*-butyl acrylate in 30 mL of CH$_2$Cl$_2$. The mixture was stirred for 3 h at room temperature. The reaction mixture was extracted with ether after 100 mL of ice-cold 0.1 N HCl was added. The organic phase was separated and evaporated to dryness, and the product was purified by spinning-disk chromatography using 10% ethyl acetate−hexane as eluant (yield 70%). For **15**: ¹H NMR (CDCl$_3$) δ 2.50−2.40 (m, 2 H), 2.32−2.28 (m, 3 H), 2.20−2.0 (m, 2 H), 1.39 (s, 9 H); ¹³C NMR (CDCl$_3$) δ 170.1, 165.9, 163.3, 123.3, 119.6, 81.1, 27.7, 26.6, 13.8; HRMS *m/z* 296.1102 (MH$^+$), calcd for C$_{12}$H$_{17}$F$_3$NO$_4$ 296.1109. For **29**: ¹H NMR (CDCl$_3$) δ 8.50−8.40 (d, 2 H), 7.66−7.61 (t, 1 H), 7.55−7.45 (t, 2 H), 2.68−2.63 (t, 2 H), 2.25−2.17 (m, 2 H), 1.41 (s, 9 H); ¹³C NMR (CDCl$_3$) δ 170.3, 162.5, 160.5, 133.8, 129.2, 128.9, 127.2, 123.5, 119.7, 81.3, 27.8, 27.6, 26.8; HRMS *m/z* 358.1272 (M$^+$), calcd for C$_{17}$H$_{19}$F$_3$NO$_4$ 358.1266.

***tert*-Butyl 2-(5-Hydroxy-4-methyl-5-(1-propynyl)-2-(trifluoromethyl)-3-oxazolyl)propionate (16), *tert*-Butyl 2-(5-Hydroxy-4-methyl-5-(phenylethynyl)-2-(trifluoromethyl)-3-oxazolyl)propionate[14] (30), and *tert*-Butyl 2-(5-Hydroxy-4-phenyl-5-(1-propynyl)-2-(trifluoromethyl)-3-oxazolyl)propionate[14] (31).** To 20 mL of a 0.01 M solution of propyne (for **16** and **31**) or phenylacetylene (**18**, for **30**) in tetrahydrofuran was added 20 mL of a 0.012 M solution of butyllithium dropwise, and the resulting solution was stirred for 1 h at 0 °C. Then 20 mL of a 0.008 M solution of the starting material (**15** for **16** and **31**; **29** for **30**) was added, and the solution was stirred for 2 h more at room temperature. A yellowish solid was obtained after workup. Products were purified by spinning-disk chromatography using a 10% ethyl acetate−hexane mixture as eluant (70% yield). For **16**: mp 118−119 °C; ¹H NMR (CDCl$_3$) δ 2.4−2.2 (m, 5 H), 2.20 (s, 3 H), 1.91 (s, 3 H), 1.43 (s, 9 H); ¹³C NMR (CDCl$_3$) δ 174.2, 81.5, 84.5, 29.0, 28.0, 27.4, 13.5, 3.3; HRMS *m/z* 336.1433 (MH$^+$), calcd for C$_{15}$H$_{21}$F$_3$NO$_4$ 336.1422. Oxazolines **16**, **30**, and **31** were directly used for the next step without further purification.

4-Hexyne-2,3-dione (9a), 1-Phenyl-3-pentyne-1,2-dione (9b), and 5-Phenyl-4-pentyne-2,3-dione (9c). Compounds **16**, **30**, and **31**, obtained from the above reactions, were dissolved in 90% formic acid and stirred for 12 h at room temperature. The mixture was then neutralized with 0.1 N NaOH and extracted with ether. Purification was carried out by spinning-disk chromatography using a 10% ethyl acetate−hexane mixture as eluant (yield 80%). For **9a**: ¹H NMR (CDCl$_3$) δ 2.38 (s, 3 H), 2.135 (s, 3 H); ¹³C NMR (CDCl$_3$) δ 194.3, 175.9, 99.4, 88.3, 23.5, 4.6; IR (neat) 2215, 1723, 1669, 1141 cm^{-1}; HRMS *m/z* 111.0457 (MH$^+$), calcd for C$_6$H$_7$O$_2$ 111.0446; UV (C$_6$H$_6$) λ$_{max}$ (ε) 360 (1520), 420 (11), 444 nm (5). For **9b**: ¹H NMR (CDCl$_3$) δ 8.06−7.99 (m, 2 H), 7.67−7.62 (m, 1 H), 7.52−7.47 (m, 2 H), 2.13 (s, 3 H); ¹³C NMR (CDCl$_3$) δ 188.6, 178.7, 134.8, 130.4, 128.8, 128.6, 100.1, 79.0, 4.7; HRMS *m/z* 173.0611 (MH$^+$), calcd for C$_{11}$H$_9$O$_2$ 173.0602; UV λ$_{max}$ (ε) 385 (42), 464 nm (sh, 12). For **9c**: ¹H NMR (CDCl$_3$) δ 7.86−7.40 (m, 5 H), 2.45 (s, 3 H); ¹³C NMR (CDCl$_3$) δ 194.2, 175.7, 133.7, 131.6, 128.4, 128.4, 99.4, 85.8, 23.6; HRMS *m/z* 129.0345 [(M − CH$_3$CO)$^+$], calcd for (C$_{11}$H$_8$O$_2$ − CH$_3$CO) 129.0340; UV: λ$_{max}$ (ε) 309 (15, 105), 428 (50), 444 nm (32).

3,3,4,4,6,8-Hexamethyl-2,7-dioxa-5,8-bicyclo[3.3.0]-octadiene (12a), 3,3,4,4,6-Pentamethyl-8-phenyl-2,7-dioxa-5,8-bicyclo[3.3.0]octadiene (12b), and 3,3,4,4,8-Pentamethyl-6-phenyl-2,7-dioxa-5,8-bicyclo[3.3.0]octadiene (12c). A solution of 0.054 g of **9a**−**c** in 50 mL of

(11) Anthracene quenching followed Stern−Volmer kinetics with $k_q\tau$ ≈ 570 M^{-1}. Anthracene is reported to quench biacetyl phosphorescence in benzene with a quenching constant (k_q) of 8.1 × 10^9 M^{-1} s^{-1}: Bäckstrom, H. L.; Sandros, K. *Acta Chem. Scand.* **1958**, *12*, 823. Using this value as an approximation of k_q here, we can estimate τ ≈ 70 ns under these conditions of bimolecular reaction with **2**.

(12) Sidman, J. W.; McClure, D. S. *J. Am. Chem. Soc.* **1955**, *77*, 6461.

(13) Rao, V. B.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1985**, *107*, 521 and references cited therein.

(14) For convenience of reference, a structure number is assigned to this compound even though no drawn structure is provided in the text.

(15) Weygand, F.; Steglich, W.; Mayer, D.; von Philipsborn, W. *Chem. Ber.* **1964**, *97*, 2023 and references cited therein.

benzene was irradiated in the presence of excess tetramethylethylene (**2**) for 2.5 h. Essentially all starting material had disappeared by the end of this time, and only one product was obtained. This was purified by spinning-disk chromatography. For **12a**: ¹H NMR (CDCl₃) δ 2.13 (s, 6 H), 1.32 (s, 6 H) 1.18 (s, 6 H); ¹³C NMR (CDCl₃) δ 145.5, 137.7, 126.0, 123.0, 99.8, 43.4, 23.4, 23.2, 12.4, 10.7; IR (neat) 2978, 2921, 1694, 1411, 1379, 1369, 1110 cm⁻¹; HRMS *m/z* 194.1294 (M⁺), calcd for C₁₂H₁₈O₂ 194.1306. For **12b**: ¹H NMR (CDCl₃) δ 7.50−7.20 (m, 5 H), 2.23 (s, 3 H), 1.31 (s, 6 H) 1.21 (s, 6 H); ¹³C NMR (CDCl₃) δ 147.8, 139.8, 131.0, 128.4, 127.4, 127.4, 124.3, 121.8, 101.5, 43.2, 23.4, 23.3, 12.6; IR (neat) 2981, 2930, 1679, 1653, 1606, 1450, 1370, 1331, 1106, 1053 cm⁻¹; HRMS *m/z* 256.1463 (M⁺), calcd for C₁₇H₂₀O₂ 256.1463. For **12c**: ¹H NMR (CDCl₃) δ 7.50−7.10 (m, 5 H), 2.15 (s, 3 H), 1.41 (s, 6 H) 1.18 (s, 6 H); ¹³C NMR (CDCl₃) δ 148.1, 139.0, 132.7, 128.4, 128.4, 127.5, 111.6, 92.2, 84.0, 51.7, 23.8, 22.3, 21.8; IR (neat) 2976, 2921, 1679, 1605, 1445, 1370, 1320, 1116, 1065 cm⁻¹; HRMS *m/z* 256.1452 (M⁺), calcd for C₁₇H₂₀O₂ 256.1463.

4,5-Diacetyl-2,2,3,3-tetramethyl-2,3-dihydrofuran (19a) and 5-Acetyl-4-benzoyl-2,2,3,3-tetramethyl-2,3-dihydrofuran (19c). Each of the above products **12a** and **12c** (50 mg) in 10 mL of hexane was stirred in the presence of silica gel (1 g) and air for 24 h. Products were purified by spinning-disk chromatography using a 10% ethyl acetate−hexane mixture as eluant (yield 75%). For **19a**: ¹H NMR (CDCl₃) δ 2.34 (s, 3 H), 2.26 (s, 3 H), 1.31 (s, 6 H) 1.13 (s, 6 H); ¹³C NMR (CDCl₃) δ 198.0, 194.5, 154.4, 127.9, 92.3, 50.6, 31.0, 28.3, 21.9, 21.6; IR (neat) 2980, 2931, 1708, 1654, 1602, 1370, 1360, 1261, 1170 cm⁻¹; HRMS *m/z* 210.1251 (M⁺), calcd for C₁₂H₁₈O₃ 210.1256. For **19c**: ¹H NMR (CDCl₃) δ 8.82−7.75 (d, 2 H), 7.60−7.47 (m, 1 H), 7.41−7.36 (t, 2 H), 2.12 (s, 3 H), 1.41 (s, 6 H) 1.17 (s, 6 H); ¹³C NMR (CDCl₃) δ 193.42, 192.2, 152.2, 139.0, 132.7, 128.4, 128.3, 111.6, 92.1, 51.7, 27.5, 22.4, 21.8; HRMS *m/z* 272.1413 (M⁺), calcd for C₁₇H₂₀O₃ 272.1410.

4,4,8-Trimethyl-6-phenyl-2,7-dioxa-5,8-bicyclo[3.3.0]-octadiene (22). 9c (0.10 g) in 50 mL of benzene was irradiated in the presence of an excess of isobutylene (**20**) for 3 h. Essentially all starting material had disappeared, and only one product was obtained, which was separated and purified by spinning-disk chromatography. For **22**: ¹H NMR (CDCl₃) δ 7.80−7.30 (m, 5 H), 4.29 (s, 2 H), 2.19 (s, 3 H), 1.35 (s, 6 H); ¹³C NMR (CDCl₃) δ 193.4, 191.7, 152.6, 138.5, 133.2,

133.2, 132.9, 128.6, 128.3, 83.7, 48.1, 27.5, 25.8; IR (neat) 2981, 2930, 1679, 1653, 1606, 1450, 1370, 1331, 1106, 1053 cm⁻¹; HRMS *m/z* 245.1179 (MH⁺) calcd for C₁₅H₁₆O₃ 245.1178.

Triplet-Sensitized Addition of 2 to 9a. Two benzene solutions, one containing only **9a** (0.05 M) and **2** (0.60 M) as described above, and the other containing, in addition, sufficient 2-benzoylnaphthalene (1.5 M) to absorb 96% of the incident light, were irradiated in a merry-go-round apparatus for 15 min. Analysis indicated formation of essentially the same amount of **12a** in each tube.

Quenching of the Addition of 2 to 9a by Anthracene. Solutions of **9a** (0.1 M) and **2** (∼0.5 M) in benzene containing various concentrations of anthracene were irradiated with light filtered first through a uranium-glass filter (λ > 340 nm) and then through a 1-cm path of a solution prepared from 750 g of NaNO₂ in 100 mL of water (λ > 400 nm)[16] and contained in a Pyrex toroidal vessel. Product **12a** was analyzed gas chromatographically using naphthalene as an internal standard. The results indicated that the formation of **12a** was quenched by anthracene and that the process followed Stern−Volmer kinetics with $k_q\tau \approx 570$ M⁻¹. When naphthalene was used as quencher, no quenching of the reaction was observed.

Supporting Information Available: Copies of ¹H or ¹³C NMR spectra are available for compounds **9a−c**, **12a−c**, **15**, **19a,c**, **22**, **28**, and **29** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(16) This filter excludes nearly all light with λ < 400 nm, permitting excitation of **9a** without excitation of anthracene. It is adapted from the original work on triplet sensitization of biacetyl (ref 11).