Cumulene Photochemistry: Photoreactions of a Strained 1,2-Cyclooctadiene

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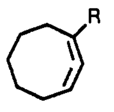
The singlet and triplet photoreactions of 1-*tert*-butyl-1,2-cyclooctadiene (1) are described. This is the first example of an isolable eight-membered ring allene and is predicted to have a bent allenic unit. Triplet reactions of 1 are phase dependent. Benzene-sensitized irradiation affords products of hydrogen abstraction at *tert*-butyl or ring carbons in vapor phase or solution phase, respectively. Direct irradiation of thoroughly degassed pentane solutions at 254 nm affords primarily 3-*tert*-butylbicyclo[3.3.0]oct-2-ene and other products that are attributed to initial excited-state 1,2-hydrogen migration to a vinylcarbene. Independent generation of this vinylcarbene gives a similar collection of products, which include an isolable bicyclo[5.1.0]oct-1(8)-ene. Irradiation of 1 in oxygenated solutions yields *tert*-butylcycloheptene (**15**), apparently through loss of carbon monoxide from an intermediate cyclopropanone. Oxidation of 1 with *m*-CPBA also leads efficiently to **15**.

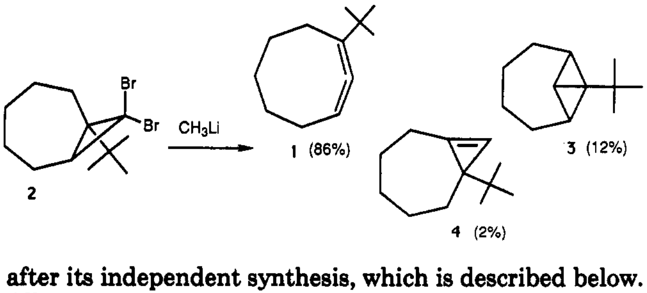
Introduction

Small-ring cyclic allenes are one fundamental class of strained organic compounds.[1] We have systematically investigated both the structural limitations[2,3] and photochemical reactions of cyclic allenes.[4-7] To further explore the effects of ring size and strain, we initially attempted[8] to study photochemical reactions of 1,2-cyclooctadiene (**1a**). These experiments proved inconclusive because of unresolved impurities in **1a** and its very facile dimerization.[9] To circumvent these problems, we synthesized buttressed allene **1**; this substance is kinetically stable because the *tert*-butyl group prevents dimerization.[3] The geometries of **1** or **1a**, optimized by molecular orbital calculations, show an allene unit that is bent by 22°. Force field calculations on **1a** predict 14 kcal/mol of total strain, only a portion of which is due to allene bending.[10] We describe here the photochemical reactions of this first example of an isolable eight-membered-ring allene.



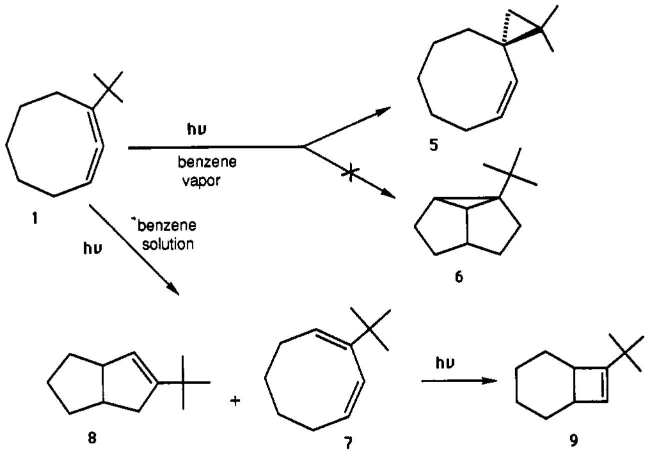
1 R = *tert*-butyl
1a R = H

Synthesis of 1-*tert*-Butyl-1,2-cyclooctadiene. Reaction of dibromocarbene adduct **2** with methyllithium yielded allene **1**, bicyclobutane **3**, and cyclopropene **4** in a ratio of 86:12:2.[3] Cyclopropene **4** was identified only after its independent synthesis, which is described below.



Allene **1** was rigorously purified by preparative gas chromatography, but proved to be very sensitive to traces of acid. The UV spectrum of **1** is consistent with a bent structure. Simple allenes show UV absorption maxima at <210 nm, but this absorption tails weakly to ca. 240 nm and the assignment of excited states has been problematic.[11] The UV spectrum of **1** still showed a short wavelength maximum (<220 nm), but the band extended to 280 nm; at 254 nm the extinction coefficient is 146. Bending the allene chromophore is predicted to lower the energy of S$_1$,[11a,d] in addition to raising the ground state, thus accounting for this bathochromic shift.

Scheme I



Exploratory Photochemistry: Triplet Reactions. Ward and Karafiath first reported that benzene is an efficient triplet sensitizer for allenes.[12a,b] In the vapor phase, the principal triplet reaction of allenes is intramolecular hydrogen abstraction, which may be preceded in some cases by closure to a cyclopropylidene.[6] In solution phase, 1,2-cyclononadiene gives primarily cycloadducts to benzene.[13] Racemization of optically active samples also occurs, which indicates that π bond rotation is occurring.[4,12d]

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[1] Review: Johnson, R. P. *Chem. Rev.* **1989**, *89*, 1111.
[2] Angus, R. O., Jr.; Schmidt, M. W.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 532.
[3] Price, J. D.; Johnson, R. P. *Tetrahedron Lett.* **1986**, *27*, 4679.
[4] Stierman, T. J.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 3971.
[5] Price, J. P.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 2187.
[6] Review: Johnson, R. P. *Org. Photochem.* **1985**, *7*, 75.
[7] Stierman, T. J.; Johnson, R. P. *J. Org. Chem.* **1990**, *55*, 1043.
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[10] Yavari, I. *J. Mol. Struct.* **1980**, *65*, 169.
[11] For discussions of allene excited states and UV spectra, see: (a) Rauk, A.; Drake, A. F.; Mason, S. F. *J. Am. Chem. Soc.* **1979**, *101*, 2284. (b) Diamond, J.; Segal, G. A. *J. Am. Chem. Soc.* **1984**, *106*, 953. (c) Elsevier, C.; Vermeer, P.; Gedanken, A.; Runge, W. *J. Am. Chem. Soc.* **1985**, *107*, 2537. (d) Lam, B.; Johnson, R. P. *J. Am. Chem. Soc.* **1983**, *105*, 7479.
[12] Use of benzene as a triplet sensitizer (E_T = 84.2 kcal/mol) for allenes: (a) Ward, H. R.; Karafiath, E. *J. Am. Chem. Soc.* **1969**, *91*, 522. (b) Ward, H. R.; Karafiath, E. *J. Am. Chem. Soc.* **1969**, *91*, 7475. (c) Karan, H. I. *J. Org. Chem.* **1981**, *46*, 2186.
[13] Berridge, J. C.; Forrester, J.; Foulger, B. E.; Gilbert, A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2425.

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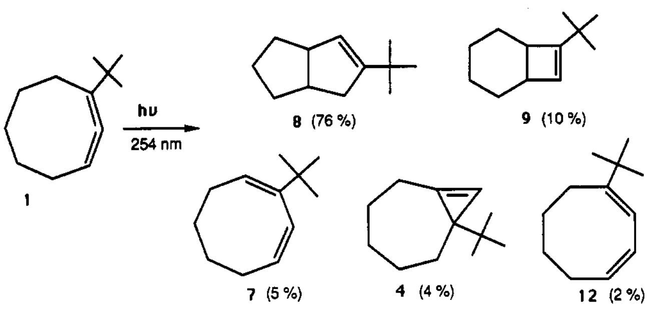
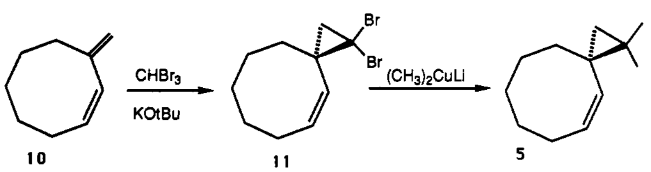
Scheme II



In the present work, triplet reactions of 1 displayed a remarkable phase dependence. Benzene-sensitized irradiation of 1 in the vapor phase resulted in a single isomeric photoproduct. The product ^{1}H NMR spectrum displayed vinyl and cyclopropyl resonances and two methyl singlets. Secure characterization as spirocycle 5 (Scheme I) was based on these data and the independent synthesis from 10 and 11, which is shown below. No evidence was found for tricyclic isomer 6, which might be an expected product based on results for other cyclic allenes.[6,12]

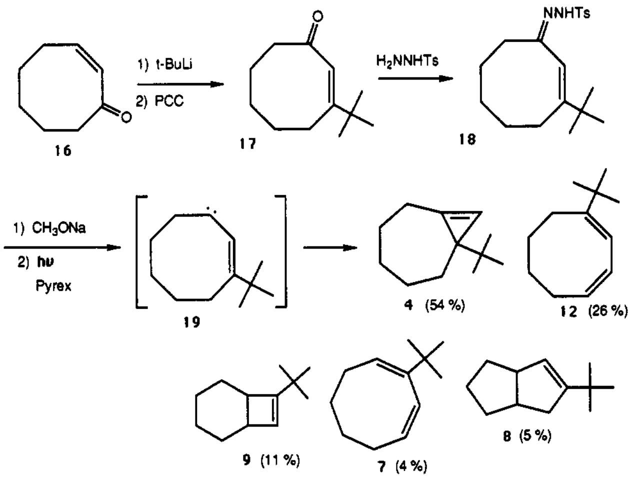


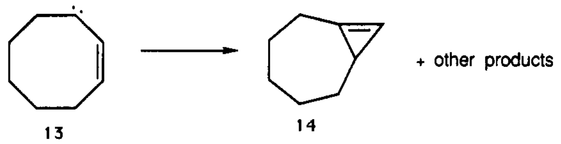
Irradiation of dilute benzene solutions of 1 at 254 nm gave two photoproducts in a 1:1 ratio. These were isolated by preparative GC and characterized as 2-*tert*-butyl-1,3-cyclooctadiene (7) and 3-*tert*-butylbicyclo[3.3.0]oct-2-ene (8). Diene 7 is a known compound[14] and is one product of the previously reported acid-catalyzed rearrangement of 1.[3] Bicyclic alkene 8 was identified by spectral data and the independent vinylcarbene synthesis described below.

Prolonged irradiation led to loss of 7, with formation of cyclobutene 9 as a secondary product; this was also formed by independent solution-phase irradiation of pure 7. This electrocyclization has ample precedent in earlier work by Fonken.[15]

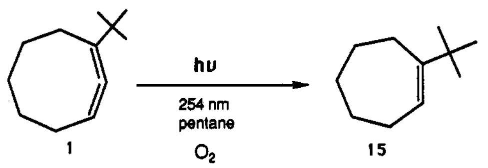
Exploratory Photochemistry: Singlet Reactions. Direct irradiation of thoroughly degassed solutions of 1 in cyclohexane at 254 nm resulted in five photoproducts (Scheme II). All were shown by capillary GC and high-field NMR analyses at increasing conversions to be primary products. The major product was 8, also noted above as a product of benzene sensitization. Arguments that 8 is derived from S_1, rather than T_1, follow from the general inefficiency of intersystem crossing in simple alkenes[16] and the very different ratio relative to the other triplet product 7. Cyclobutene 9 was unexpected as a singlet photoproduct; there are no previous allene to cyclobutene photochemical conversions.[6,17] The ^{1}H NMR (δ 6.45, singlet) and IR (1765 cm^{-1}) spectra of 4 provide secure characterization as a cyclopropene derivative. The formation of 4 has ample precedent in earlier studies on cyclic allene chemistry.[4-6] It is noteworthy that this is the first reported example of an *isolable* bicyclo[5.1.0]oct-1(8)-ene.[18] Billups has trapped 14, the parent cyclopropene,[19] and we have found this compound can be prepared from vinylcarbene 13.[8]

Scheme III





Irradiation of pentane solutions of 1 that were intentionally not degassed, or only briefly degassed, yielded an unexpected and remarkable reaction. At low-conversion (<20%), *the major observed product was tert-butylcycloheptene* (15), identical in all respects with samples on hand from the synthesis of 1. Formally, this product results from the loss of a carbon atom. At higher conversion, the other products shown in Scheme II were observed. More rigorous deoxygenation prior to irradiation virtually eliminated this reaction. Mechanistic studies are described below.



Independent Vinylcarbene Generation. One potential intermediate in the singlet reactions of 1 is vinylcarbene 19 (Scheme III).[4-6,17] A suitable precursor is tosylhydrazone 18, which was prepared as shown. Reaction of cyclooctenone with *t*-BuLi followed by oxidative allylic transposition[20] gave 17 in 6% overall yield; this was easily converted to 18. Irradiation of the sodium salt of 18 through Pyrex ($\lambda > 290$) until the red diazo intermediate had completely faded gave a 44% yield of the products shown in Scheme III. The most unusual products here are 7 and 9, which apparently result from 1,4-hydrogen migration and insertion, respectively. Formation of 4 and 12 by closure and 1,2-H shift, respectively, is well precedented,[4,5,7] as is transannular insertion to 8.

Discussion

Triplet Reaction Mechanisms. Aside from π bond rotations,[4,12d] the principal known reaction of allene triplet states is hydrogen abstraction.[3-6,12] In some cases, the evidence supports initial closure to a triplet cyclopropylidene.[4,5,12a-c] Rotation to a planar triplet allene is

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[14] Zountsas, V. J.; Kreuzer, M.; Meier, H. *Angew. Chem.* **1983**, *95*, 638.

[15] Nebe, W. J.; Fonken, G. J. *J. Am. Chem. Soc.* **1969**, *91*, 522.

[16] Kropp, P. J. *Org. Photochem.* **1979**, *5*, 1.

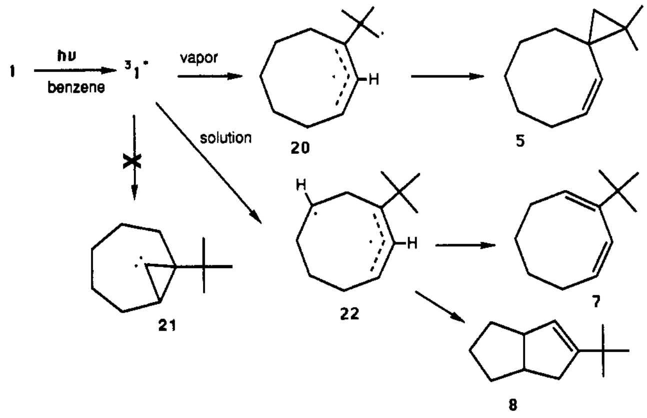
[17] Steinmetz, M. G.; Srinivasan, R.; Leigh, W. J. *Rev. Chem. Intermed.* **1984**, *5*, 57.

[18] Billups, W. E.; Haley, M. M.; Lee, G. A. *Chem. Rev.* **1989**, *89*, 1147.

[19] Billups, W. E. Unpublished results, cited in ref 18.

[20] Dauben, W. G.; Michno, D. M. *J. Org. Chem.* **1977**, *42*, 682.

Scheme IV



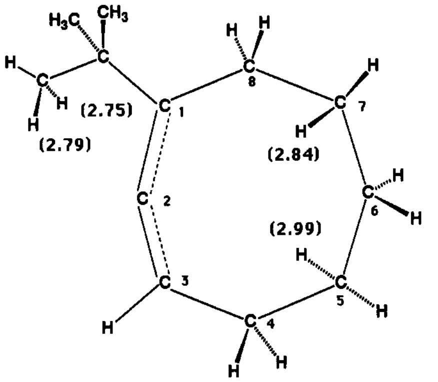


Figure 1. MNDO-optimized geometry for triplet 1. Numbers in parentheses are distances to C2.

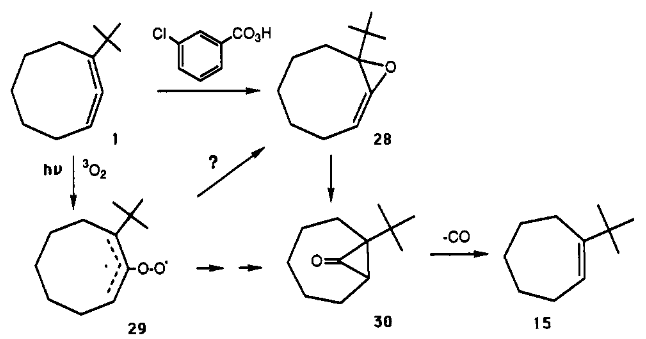
a lower energy pathway and can also explain many observed results. On the basis of the observed isomeric products, triplet reactions of 1 follow the two hydrogen abstraction modes shown in Scheme IV. Vapor-phase reaction must proceed through diradical 20, while in the solution phase selective abstraction at C7 would yield 22, which is the logical precursor to observed products 7 and 8. Neither observed product is consistent with the intermediacy of cyclopropylidene 21, unless the cyclopropane ring reopens at some point.

Figure 1 shows the geometry of triplet 1, predicted by calculations with the MNDO method.[21] The optimized structure (H_f = 46.9 kcal/mol) shows a nearly planar allene.[22] Significantly, the two hydrogens closest to the allene central carbon are the observed sites of abstraction. We ascribe the regioselective ring hydrogen abstraction to this skewed structure, which places C7 somewhat closer than C5.

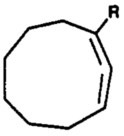
The observed phase dependence of triplet reactions is remarkable. One simple explanation is that low-pressure vapor-phase reaction involves a vibrationally "hot" triplet species and thus follows the higher energy pathway, i.e., abstraction to give the least stable diradical. In solution, a vibrationally "cold" triplet is more selective. This is similar to the temperature-dependent change in atom abstraction selectivity, which is observed for some radicals and carbenes.[23]

Singlet energy transfer from benzene to 1 is possible, but seems inconsistent with the absence of other singlet-derived products.

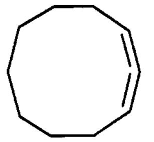
Scheme V



Singlet Reaction Mechanisms. 1,2-Hydrogen migration is commonly observed for allene singlet excited states.[3-6,24,25] In our earlier studies, we found that singlet reactions of 1,2-cyclononadiene (23)[4] and 1,2-cyclodecadiene (25)[5] yield primarily cyclopropenes, possibly through a concerted mechanism. Simple alkyl substitution in 24 diverts the reaction toward products characteristic of vinylcarbene intermediates.[7] In the present case, we believe the correspondence of vinylcarbene and S_1-derived products implicates 19 (Scheme III) as an intermediate in the singlet photochemistry of 1. What is interesting, although certainly precedented, is that two reactions with a common intermediate should give substantially different product distributions. We attribute these differences to the low barriers (<5 kcal/mol) that are expected for singlet vinylcarbene reactions[26] and slow equilibration of conformations of 19. Inspection of models shows that, if one begins with the predicted structure for 1,[3] 1,2-H migration (C3 to C2) and bending can result in *syn*-vinylcarbene conformation 26 with minimal motion. This conformation is necessary for the transannular insertion that leads to 8, the observed major product. The vinylcarbene diazo precursor would have a very different eight-membered-ring conformation. Photolysis would yield an initial vinylcarbene geometry close to 27, which is favorable both for 1,2-hydrogen shift (to 12) and closure to cyclopropene 4.



23 R=H
24 R=CH_3



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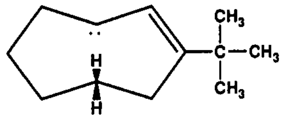

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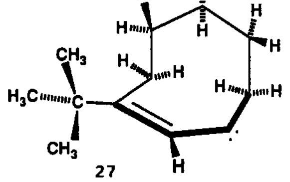

27

Clearly, the *most* unusual reaction of allene 1 is photochemical carbon loss to give *tert*-butylcycloheptene (15). This carbon loss has some precedent in allene photoreactions reported earlier by Steinmetz.[17] In these cases the mechanism remained obscure; loss of atomic carbon would be highly endothermic. This reaction proved en-

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[21] Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

[22] The predicted energy difference between 1 (MNDO H_f = 24.6 kcal/mol[3]) and the triplet is 22.3 kcal/mol. We found earlier[2] that MNDO substantially underestimates the rotational barrier in allene.

[23] Giese, B. *Acc. Chem. Res.* **1984**, *17*, 438.

[24] Klett, M. W.; Johnson, R. P. *Tetrahedron Lett.* **1983**, *24*, 1107. Klett, M. W.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 3963.

[25] Steinmetz, M. G.; Stark, E. J.; Yen, Y. P.; Mayes, R. T.; Srinivasan, R. *J. Am. Chem. Soc.* **1983**, *105*, 7209. Steinmetz, M. G.; Mayes, R. T.; Yang, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 3518.

[26] (a) Honjou, N.; Pacansky, J.; Yoshimine, M. *J. Am. Chem. Soc.* **1985**, *107*, 5332. (b) Yoshimine, M.; Pacansky, J.; Honjou, N. *J. Am. Chem. Soc.* **1989**, *111*, 2785.

tirely mystifying until its oxygen dependence (vide supra) was established. Evidence for the mechanism was provided by a simple experiment: Treatment of allene **1** (Scheme V) with 1 equiv of *m*-chloroperbenzoic acid gave an 86% yield of **15**. When the reaction was monitored by ^{1}H NMR spectroscopy, a vinyl resonance attributable to allene oxide **28** (δ 5.97, dd, J = 5.9, 3.5 Hz) appeared. This intermediate disappeared quickly, with simultaneous formation of **15**. Precedent for this unusual reaction is found in two earlier reports that epoxidation of 1,2-cyclononadiene gives cyclooctene as a major product.[27] We thus believe that carbon loss from **1** proceeds through addition of oxygen to S_1 (**1**) to give either **28** or **30**. The allene oxide–cyclopropanone rearrangement (**28** → **30**) is well precedented.[27,28] Spontaneous thermal decarbonylation of **30** completes the mechanism of carbon loss.

Photochemical epoxidation of alkenes was reported earlier by Kropp and co-workers.[29] A hydroperoxy radical was suggested as the oxygen-donating species.

Efficient quenching of an allene singlet state (presumed lifetime $<10^{-8}$ s) by a low concentration of dissolved oxygen is not possible, and we can only speculate that some preassociation between $^{3}O_2$ and **1** may exist. This would explain the predominance of carbon loss at low conversion, while other reactions arise as oxygen is depleted.

Conclusions

1-*tert*-Butyl-1,2-cyclooctadiene (**1**) is the first example of an isolable eight-membered ring allene, with a strongly bent allene unit.[1,3] Its triplet photochemistry, studied by benzene sensitization, shows a novel phase dependence for hydrogen abstraction selectivity and is consistent with a planar triplet intermediate, rather than closure to a cyclopropylidene. As in previous studies, 1,2-hydrogen migration to give carbene **19** is the dominant singlet-state reaction; the intermediacy of a vinylcarbene is supported by its independent generation. One of the products is the first reported example of an isolable bicyclo[5.1.0]oct-1-(8)-ene. No evidence was seen for 1,3-hydrogen migration to a cyclooctyne. The most novel reaction is loss of the allene central carbon atom when **1** is irradiated in the presence of oxygen or oxidized with *m*-CPBA. Carbon loss also occurs upon epoxidation of 1,2-cyclononadiene, and this seems likely to be a general reaction of strained cyclic cumulenes. With the exception of this last reaction, the role of strain in photoreactions of **1** probably is less important than the ring size and alkyl substitution.

Experimental Section

General. NMR spectra were measured on a 300-MHz spectrometer with TMS as reference. Gas chromatographic analyses were performed on a 15-m methyl phenyl siloxane capillary column. Preparative separations were performed with glass-lined injector and glass columns. Melting points are uncorrected. Procedures for photochemical experiments have been previously described.[4]

Preparation of 8,8-Dibromo-1-*tert*-butylbicyclo[5.1.0]octane (2). To 1-*tert*-butylcycloheptene[30] (10.6 g, 69.7 mmol) and potassium *tert*-butoxide (15.7 g, 140 mmol) in 150 mL of pentane at 0 °C was added 32.9 g (130 mmol) of bromoform. After 8 h and standard workup, unreacted material was distilled (35–40 °C (0.10 Torr)). Chromatography (silica gel, 50 × 3 cm, eluting with hexanes) gave an oil that was taken up in pentane and stored overnight at −20 °C to give 8.26 g (37%) of crystals of **2**, mp 46–47 °C: ^{1}H NMR (CDCl$_3$) δ 2.47–2.34 (m, 1 H), 2.34–2.22 (m, 1 H), 1.90 (t, J = 8.5 Hz, 1 H), 1.80–1.61 (m, 6 H), 1.51–1.33 (m, 1 H), 1.27 (t, J = 12.4 Hz, 1 H), 1.20 (s, 9 H); ^{13}C NMR δ 52.03, 42.22, 36.82, 36.66, 34.23, 32.48, 31.19, 29.41, 29.25, 28.34; HRMS *m/z* 323.9917, calcd 323.9912.

1-*tert*-Butyl-1,2-cyclooctadiene (1). To **2** (4.91 g, 15.2 mmol) in 25 mL of pentane at 0 °C was added methyllithium (18.0 mmol) in ether. After standard workup, distillation (pot <60 °C (0.05 Torr)), afforded 2.29 g (92%) of colorless oil. Capillary GLC analysis (80 °C) showed three major products, isolated on preparative scale (25% Carbowax on Chromosorb W, 5 ft × 0.25 in., 110 °C) and identified as **1** [yield 85%; oil; ^{1}H NMR (CDCl$_3$) δ 5.30–5.22 (m, 1 H), 2.25–2.12 (m, 2 H), 2.00–1.77 (m, 2 H), 1.66–1.30 (m, 6 H), 1.07 (s, 9 H); ^{13}C NMR δ 202.21, 117.73, 94.44 (J_{CH} = 166 Hz), 33.23, 29.28 (double intensity), 28.79, 28.24, 27.60, 27.24; IR (neat) 1942 cm^{-1}; mass spectrum *m/z* (relative intensity) 164 (M^{+}, 5), 149 (15), 136 (4), 121 (36), 107 (60), 93 (87), 79 (100), 67 (58), 57 (61); HRMS *m/z* 164.1565, calcd 164.1565; UV (cyclohexane), shoulder 235 nm (ϵ = 978) (ϵ_{254} = 146)]; 7-*tert*-butylbicyclo[5.1.0]oct-1(8)-ene (**4**) [yield 2%; spectral data are given below]; and 1-*tert*-butyltricyclo[5.1.1.0^{2,8}]octane (**3**) [yield 12%; oil; ^{1}H NMR (CDCl$_3$) δ 2.66–2.61 (m 2 H), 1.73–1.66 (m, 4 H), 1.31 (pentet, J = 2.9 Hz, 4 H), 1.04 (t, J = 3.4 Hz, 1 H), 0.96 (s, 9 H); ^{13}C NMR δ 48.98, 33.25, 32.00, 29.44, 29.08, 27.30, 14.62].

Acid-Catalyzed Rearrangement of 1. To 55 mg of GLC-purified **1** in 15 mL of benzene was added 10 mg of *p*-toluenesulfonic acid. After 4 h, passage through a short alumina column and concentration gave 49 mg (88%) of colorless oil. Capillary GLC indicated complete conversion to two products, isolated on a preparative scale (10 ft × 0.25 in., 15% SE-30 on Chromosorb W, 140 °C) and identified[13] as 2-*tert*-butyl-1,3-cyclooctadiene (**7**) [yield 87%; ^{1}H NMR (CDCl$_3$) δ 5.95 (d, J = 11.2 Hz, 1 H), 5.75 (dt, J = 11.2 Hz, 7.3 Hz, 1 H), 5.49 (t, J = 8.1 Hz, 1 H), 2.02 (m, 4 H), 1.36 (m, 4 H), 1.04 (s, 9 H); ^{13}C NMR δ 145.80, 131.76, 126.07, 122.28, 34.93, 29.39, 28.26, 27.84, 27.70, 22.73; UV (cyclohexane) λ_{max} 220 nm ($\epsilon = 1.12 \times 10^{5}$)] and 1-*tert*-butyl-1,3-cyclooctadiene (**12**) [yield 13%; ^{1}H NMR (CDCl$_3$) δ 5.79 (d, J = 4.4 Hz, 1 H), 5.71 (dd, J = 11.7 Hz, 4.4 Hz, 1 H), 5.59 (dt, J = 11.7 Hz, 5.9 Hz, 1 H), 2.31–2.25 (m, 2 H), 2.13 (dd, J = 10.7 Hz, 5.9 Hz, 2 H), 1.60–1.42 (m, 4 H); ^{13}C NMR δ 149.09, 130.48, 126.40, 119.74, 36.85, 29.99, 29.76, 27.24, 26.24, 22.71; UV (cyclohexane) λ_{max} 234 nm (ϵ = 5950)].

Benzene-Sensitized Vapor-Phase Irradiation of 1. Allene **1** (125 mg) and benzene (170 mg) were placed in a 3.7-L Vycor tube. The bottom portion was cooled with dry ice, and the system was evacuated to ca. 0.15 Torr and backflushed with nitrogen three times. After the final evacuation, the tube was allowed to warm to room temperature, placed in a Rayonet reactor fitted with 254-nm lamps, and irradiated for 64 h. The reaction vessel was then cooled to −78 °C and vented to nitrogen, and the product was collected with pentane. The pentane solution was filtered through neutral alumina and concentrated to give 92 mg (74%) of a colorless oil. Analysis by GLC and ^{1}H NMR indicated 66% conversion to one photoproduct, identified as **5**.

1,1-Dimethylspiro[2.7]dec-4-ene (5). To potassium *tert*-butoxide (5.60 g, 50.0 mmol) and 3-methylene-1-cyclooctene (**10**; 5.00 g, 40.9 mmol) in 100 mL of pentane at 0 °C was added 10.4 g (41.4 mmol) of bromoform. After 10 h, workup and distillation gave dibromide **11** as an oil: bp 95–102 °C (0.05 Torr); yield 9.41 g (78%); ^{1}H NMR (CDCl$_3$) δ 5.77 (dt, J = 10.3 Hz, 8.2 Hz, 1 H), 5.60 (d, J = 10.3 Hz, 1 H), 2.26–2.18 (m, 2 H), 1.88–1.52 (m, 10 H); ^{13}C NMR (CDCl$_3$) δ 133.94, 131.06, 39.86, 37.08, 32.68, 27.84, 26.14, 25.66, 24.99; HRMS *m/z* 293.94427, calcd 293.94418.

Dimethyl cuprate was prepared by the method of Corey and Posner.[31] To copper(I) iodide (2.23 g, 11.7 mmol) in ether at 0 °C was added methyllithium (23.4 mmol) in ether. Dibromide **11** (560 mg, 1.93 mmol) was added. After 24 h, standard workup gave 214 mg (56%) of oil, further purified by preparative GLC: ^{1}H NMR (CDCl$_3$) δ 5.61–5.47 (m, 2 H), 2.30–2.11 (m, 2 H), 1.65–1.42 (m, 8 H), 1.16 (s, 3 H), 1.04 (s, 3 H), 0.36 (d, J = 3.7

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Hz, 1 H), 0.29 (d, J = 3.7 Hz, 1 H); ^{13}C NMR δ 134.30, 131.28, 36.74, 29.14, 28.39, 27.59, 25.94, 25.64 (double intensity), 24.06, 21.79, 21.54; HRMS *m/z* 164.15644, calcd 164.15650.

Benzene-Sensitized Solution-Phase Irradiation of 1. Allene 1 (66 mg) and 20 mL of benzene in a quartz tube were degassed 3 h with argon, irradiated (Rayonet, 254-nm lamps), and monitored by capillary GLC (80 °C). At low conversions (<20%), two primary photoproducts (ratio 1:1) were observed. Isolation by preparative GLC (20% Carbowax) gave *cis*-3-*tert*-Butylbicyclo[3.3.0]oct-2-ene (8) [yield 11%; ^{1}H NMR, 5.10 (s, 1 H), 3.07–3.20 (m, 1 H), 2.68–2.52 (m, 2 H), 2.00 (d, J = 13.7 Hz, 1 H), 1.73–1.20 (m, 6 H), 1.02 (s, 9 H); ^{13}C NMR δ 152.45, 124.66, 50.24, 40.51, 39.76, 35.75, 32.74, 29.34, 25.17; IR (neat) 1653 cm^{-1}; HRMS *m/z* 164.1559, calcd 164.1565; 7 (10%)] and 1 (79%). At higher conversions, a new product was identified as 7-*tert*-butylbicyclo[4.2.0]oct-7-ene (9).

Benzene-Sensitized Solution-Phase Irradiation of 2-*tert*-Butyl-1,3-cyclooctadiene (7). GLC-purified 7 (44 mg) in 20 mL of benzene was degassed 3 h with argon and was irradiated (Rayonet, 254 nm) with monitoring by GLC. One major photoproduct was observed, comprising greater than 96% of products at a conversion of 46%. This was isolated by GLC (10% SE-30 on Chromosorb W) and identified as 9: ^{1}H NMR (CDCl$_3$) δ 5.69 (s, 1 H), 2.77 (dd, J = 11.0 Hz, 6.2 Hz, 1 H), 2.51 (dd, J = 11.0 Hz, 5.4 Hz, 1 H), 1.72–1.49 (m, 5 H), 1.42–1.31 (m, 3 H), 1.02 (s, 9 H); ^{13}C NMR δ 162.19, 127.50, 40.32, 36.30, 33.26, 28.40, 25.27, 24.78, 19.05, 18.96; HRMS *m/z* 164.1565, calcd 164.1565.

Direct Irradiation of 1-*tert*-Butyl-1,2-cyclooctadiene (1). GLC-purified 1 (41 mg) in 20 mL of cyclohexane was degassed with argon for 12 h. Irradiation (Rayonet, 254 nm) for 8 h gave 38% conversion to six photoproducts identified as 8 (76%), 9 (10%), 7 (5%), 4 (4%), 12 (2%), and 1-*tert*-butylbicyclo[5.1.0]oct-2-ene (<1%). Product ratios were determined by ^{1}H NMR integration. Similar results were obtained by GLC. At different conversions (12, 29, 51, and 71%) the reaction composition remained essentially unchanged. These products constituted greater than 97% of the mixture.

3-*tert*-Butyl-2-cycloocten-1-one (17). The general procedure of Dauben and Michno was employed.[20] To 2-cycloocten-1-one (13.9 g, 81 mmol) in pentane (150 mL) at 0 °C was added 10.0 g (156 mmol) of *tert*-butyllithium in pentane. After 8 h at 25 °C, quenching with 2-propanol, and standard workup, the crude 1-*tert*-butyl-2-cycloocten-1-ol was added to pyridinium chlorochromate (51.8 g, 240 mmol) in 0.5 L of CH$_2$Cl$_2$. Following workup, purification was by chromatography (silica gel, 70 × 2 cm, eluting with 20% ether/hexanes, 200-mL fractions). Fractions 4–6 gave 7 (860 mg, 5.9%, >98% purity): oil; bp 75–78 °C (0.10 Torr); ^{1}H NMR (CDCl$_3$) δ 6.16 (s, 1 H), 2.75 (t, J = 7.1 Hz, 2 H), 2.69 (t, J = 6.8 Hz, 2 H), 1.78–1.68 (m, 2 H), 1.68–1.57 (m, 2 H), 1.56–1.47 (m, 2 H), 1.10 (s, 9 H); ^{13}C NMR (CDCl$_3$) δ 204.67, 162.83, 128.41, 42.28, 38.56, 28.73, 28.02, 25.59, 23.55, 23.33; IR (neat) 1649, 1610 cm^{-1}; HRMS *m/z* 180.15131, calcd 180.15142.

3-*tert*-Butyl-2-cycloocten-1-one *p*-Toluenesulfonhydrazone (18). To enone 17 (440 mg, 2.44 mmol) in 10 mL of benzene was added 470 mg (2.50 mmol) of *p*-toluenesulfonhydrazide. After 8 h, pentane (10 mL) was added, and the cloudy solution was stored at −20 °C for 48 h. The tosylhydrazone (436 mg, 51%) was obtained as white crystals: mp 98–101 °C; ^{1}H NMR (CDCl$_3$) δ 7.80 (d, J = 7.8 Hz, 2 H), 7.35 (s, 1 H, 7.29 (d, J = 7.8 Hz, 2 H), 5.42 (s, 1 H), 2.41 (s, 3 H), 2.35 (t, J = 5.9 Hz, 2 H), 1.80 (m, 2 H), 1.58 (br s, 3 H), 1.43–1.30 (m, 3 H), 1.09 (s, 9 H); ^{13}C NMR (CDCl$_3$) δ 160.27, 158.36, 143.67, 129.37, 128.30, 127.91, 113.32, 37.71, 37.29, 29.56, 28.13, 27.16, 26.97, 24.74, 21.50. Anal. Calcd for $C_{15}H_{26}N_2O_2S$: C, 65.48, H, 8.10, N, 8.04. Found: C, 66.09, H, 8.17, N, 7.65.

Photolysis of the Sodium Salt of 18. The tosylhydrazone (360 mg, 1.03 mmol) and 40 mL of dry THF, in a Pyrex flask, was degassed (Ar, 2 h). Sodium methoxide (301 mg, 5.10 mmol) was added, and the solution was irradiated (Rayonet, 300 nm) for 6 h. The solution was poured into pentane (100 mL) and washed (water, 5 × 100 mL). The pentane was filtered through alumina and concentrated to give an oil (74 mg, 44%). GLC (80 °C) indicated five products, which were isolated by preparative GLC (15% SE-30 on Chromosorb W, 10 ft × 0.25 in., 140 °C) and identified as 7-*tert*-butylbicyclo[5.1.0]oct-1(8)-ene (4) [yield 54%; oil; ^{1}H NMR (CDCl$_3$) δ 6.45 (s, 1 H), 2.70 (dt, J = 13.5, 4.4 Hz, 1 H), 2.38 (td, J = 11.5, 6.3 Hz, 1 H), 1.92–1.85 (m, 1 H), 1.78 (td, J = 11.5, 6.3 Hz, 1 H), 1.68 (dd, J = 14.4, 6.6 Hz, 1 H), 1.53 (dt, J = 13.6, 3.9 Hz, 1 H), 1.40 (dt, J = 13.6, 3.9 Hz, 1 H), 1.29 (dd, J = 12.2, 5.9 Hz, 1 H), 1.14 (q, J = 11.6 Hz, 1 H), 0.95–0.84 (m, 1 H), 0.81 (s, 9 H); ^{13}C NMR (CDCl$_3$) δ 129.34, 104.16, 35.12, 33.70, 33.18, 29.75, 29.20, 29.07, 27.65, 25.70; IR (neat) 1765 cm^{-1}; HRMS *m/z* 164.15668, calcd 164.15650]; 12 (26%); 9 (11%); 8 (5%); and 7 (4%).

Reaction of 1 with *m*-Chloroperbenzoic Acid. To GLC-purified 1 (7.0 mg, 0.043 mmol) in 0.5 mL of CDCl$_3$ in a NMR tube was added 7.4 mg (0.043 mmol) of *m*-chloroperbenzoic acid. After 45 min, the ^{1}H NMR spectrum displayed two vinyl resonances in the approximate ratio of 1:1, assigned to 1-*tert*-butyl-1,2-cyclooctadiene oxide (28) [partial ^{1}H NMR δ 5.97 (dd, J = 5.9 Hz, 3.5 Hz)] and 1-*tert*-butylcycloheptene (15) [partial ^{1}H NMR δ 5.67 (t, J = 6.1 Hz). After 5 h more, NMR showed nearly complete conversion to 15.

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Supplementary Material Available: 300-MHz ^{1}H NMR spectra for selected new compounds (8 pages). Ordering information is given on any current masthead page.