# Determination of the Triplet Lifetimes of 1,3-Cyclopentadiyl Biradicals Derived from the Photodenitrogenation of Azoalkanes with Time-Resolved Photoacoustic Calorimetry

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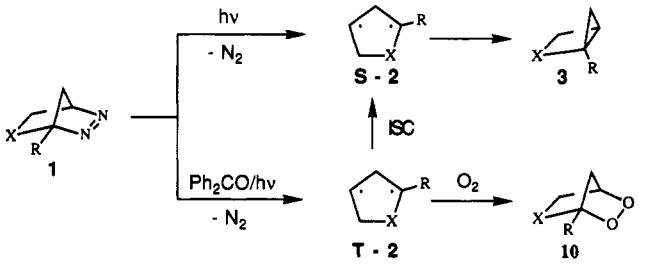
The triplet lifetime of the parent 1,3-cyclopentanediyl (**2a**) and the 4-methylene and the 1-phenyl derivatives **2b** and **2c** were determined by time-resolved photoacoustic calorimetry (PAC). For the biradical **2b**, PAC was the only suitable method to date for determining its hitherto inaccessible triplet lifetime. A comparison with results for biradicals **2a,c** obtained in earlier studies shows that PAC is a reliable method for measuring triplet lifetimes of biradicals. The effect on the triplet lifetimes of allyl and benzyl conjugation at one radical center in **2b,c** proved to be insignificant. In view of the large enhancement of the biradical lifetime as the result of benzylic conjugation at both radical sites, as in the diphenyl derivative **2d**, the present results imply that the biradicals **2b,c** are still flexible enough to enable effective intersystem crossing through pyramidalization. The much larger (ca. 200-fold) triplet lifetime of biradical **2b** compared to its *gem*-dimethyl derivative **2e** suggests that geminal substitution is a general phenomenon for the effective reduction of the lifetimes of triplet biradicals through changes in the singlet–triplet energy gap.

## Introduction

Biradicals are the focus of numerous mechanistic studies.[1] Especially popular are the 1,3-cyclopentanediyl biradicals, which are generated conveniently and efficiently by denitrogenation of cyclic azoalkanes (Scheme I) and have received recently much attention.[1f-j] The corresponding triplet biradicals (T) are obtained by benzophenone-sensitized photolyses of the azoalkanes, whose lifetimes and the factors which govern them are of major concern in mechanistic discussions. Besides time-resolved spectroscopy (most frequently UV detection,[1e] but also ESR,[1d] IR,[1i] Raman,[1j] etc.) indirect methods such as trapping with dioxygen (competition kinetics)[1h] and nitroxides[1k] or "free radical clocks"[1f,2] have been employed to detect the transient triplet biradicals and to estimate their lifetimes. The latter methods have the advantage that biradicals, which lack a chromophore and thereby are "invisible" for transient spectroscopy, can be studied; however, detailed chemical analysis of the products and of the kinetics are necessary to extract the desired lifetime data, and the results have to rely on some assumption about the transferability of a benchmark rate constant (of ring opening or oxygen trapping).

**Scheme I**




**a:** X = $CH_2$, R = H; **b:** X = >C=$CH_2$, R = H; **c:** X = $CH_2$; R = Ph

Time-resolved photoacoustic calorimetry (PAC)[3] is a direct method to determine lifetimes of high-energy transient intermediates, which does not require a chromophore for spectroscopic detection. We have determined the lifetime of the triplet biradicals **2a–c** in solution by PAC to assess the effects of substituting one of the localized radical centers in the parent 1,3-cyclopentanediyl (**2a**) by a conjugating allyl or a benzyl function as in **2b,c** and present herein our results.

Some aspects of the biradical **2b** have already been examined under matrix isolation[4] and by dioxygen trapping;[5] thus, ESR studies[4] have revealed a triplet ground state for **2b**, while the singlet–triplet energy gap was estimated to be 2.7 kcal/mol and the activation barrier for intersystem crossing 2.2 kcal/mol.[5]

## Results

**Synthesis of the Azoalkanes.** Azoalkane **1a** was readily available by following the published procedure.[6a]

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(1) (a) Dauben, W. G.; Salem, L.; Turro, N. *Acc. Chem. Res*, **1975**, *8*, 41. (b) Wirz, J. *Pure Appl. Chem.* **1984**, *56*, 1289. (c) Borden, W. T., Ed. *Diradicals*; Wiley-Interscience: New York, 1982. (d) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688. (e) Caldwell, R. A. In *Kinetics and Spectroscopy of Biradicals and Carbenes*; Platz, M. S., Ed.; Plenum: New York, 1990. (f) Engel, P. S., Culotta, A. M. *J. Am. Chem. Soc.* **1991**, *113*, 2686 and references cited therein. (g) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99. (h) Adam, W.; Grabowski, S.; Wilson, R. M. *Acc. Chem. Res*, **1990**, *23*, 165 and references cited therein. (i) Fisher, J. J.; Penn, J. H.; Döhnert, D.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 1715. (j) Adams, J. S.; Weisman, R. B.; Engel, P. S. *J. Am. Chem. Soc.* **1990**, *112*, 9115. (k) Adam, W.; Bottle, S. *Tetrahedron Lett.* **1991**, 1405. Adam, W.; Bottle, S.; Finzel, R.; Kammel, T.; Peters, E. M.; Peters, K.; von Schnering, H. G.; Walz, L. *J. Org. Chem.* **1992**, *56*, 982.

(2) (a) Adam, W.; Günther, E.; Hössel, P.; Platsch, H.; Wilson, R. M. *Tetrahedron Lett.* **1987**, 4407. (b) Adam, W.; Grabowski, S.; Scherhag, G. *Tetrahedron Lett.* **1988**, 5637. (c) Griller, R.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

(3) (a) Braslavsky, S. E.; Heibel, G. E. *Chem. Rev.* **1992**, *92*, 138. (b) Caldwell, R. A.; Melton, L. A.; Ni, T. *J. Am. Chem. Soc.* **1989**, *11*, 457. (c) Goodman, J. L.; Herman, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 2681.

(4) Dowd, P.; Ham, S. W.; Chang, W.; Partian, C. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 13. (b) Dowd, P.; Ham, S. W.; Chang, W. J. *J. Am. Chem. Soc.* **1989**, *111*, 4130.

(5) (a) Roth, W. R.; Bauer, F.; Braun, K.; Offerhaus, R. *Angew. Chem.* **1989**, *101*, 1092; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1056. (b) Roth, W. R.; Bauer, F.; Breuckmann, R. *Chem. Ber.* **1991**, *124*, 2041.

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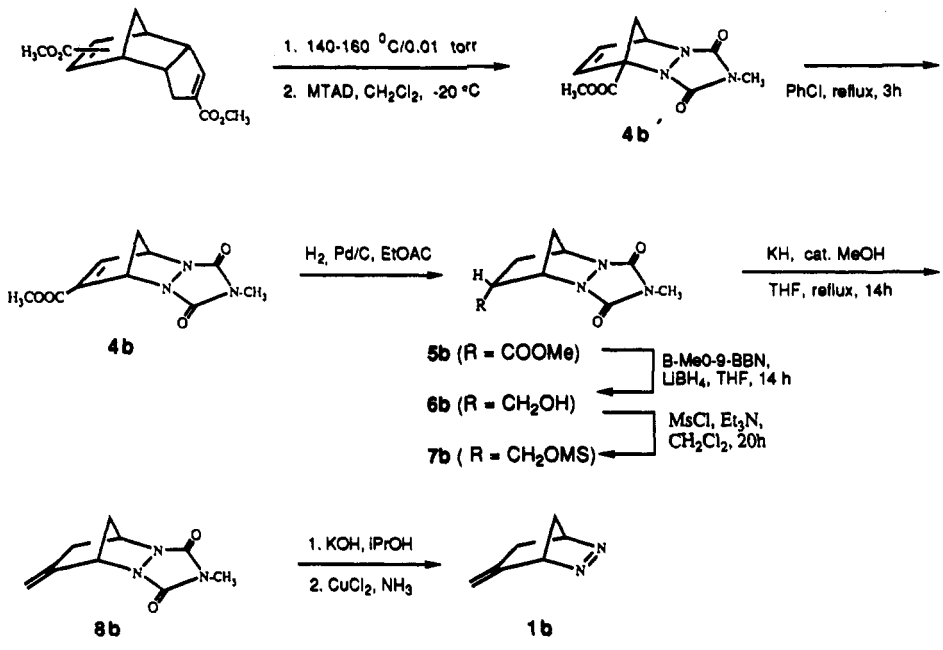
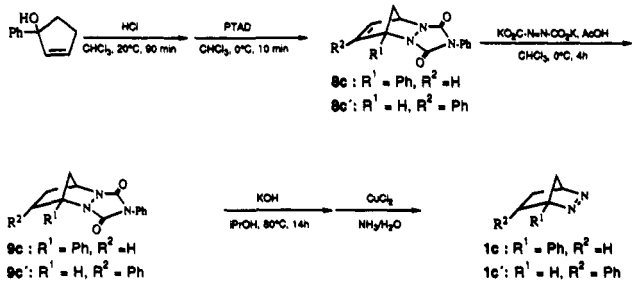
**Scheme II**



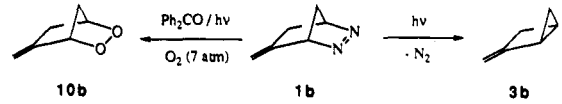

**Scheme III**




The preparation of the 5-methyleneazoalkane **1b** was already reported.[4] In view of the low yield of this procedure, an alternative synthetic methodology was sought (Scheme II). Thus, the Diels–Alder reaction[7] of *N*-methyl-1,2,4-triazoline-3,5-dione (MTAD) with 1-(carboxymethoxy)cyclopentadiene (obtained by cracking its dimer)[8] at low temperatures afforded the crystalline adduct **4b'** in good yields. The latter rearranged completely to the isomer **4b** in refluxing chlorobenzene. Hydrogenation yielded the methyl ester **5b** quantitatively, which was converted to the urazole **8b** according to the literature procedure.[4] Application of the standard hydrolysis/oxidation sequence[6] to the urazole afforded the azoalkane **1b** in 86% yield.

To prepare the azoalkane **1c**, *N*-phenyl-1,2,4-triazoline-3,5-dione (PTAD) was allowed to react with phenylcyclopentadiene,[9,10] which was obtained as a mixture of the 1,2 regioisomers by dehydration of 1-phenyl-2-cyclopenten-1-ol[10] (Scheme III). The Diels–Alder adducts **8c,c'** were hydrogenated with diimide and the resulting urazoles **9c,c'** converted to the azoalkanes **1c,c'** by the standard procedure.[6] The desired isomer **1c** was obtained in pure form by chromatographic separation.

**Photolyses.** Direct photolysis and benzophenone-sensitized photolyses of azoalkane **1b** under an argon gas atmosphere yielded bicyclopentane **3b**[5,11] as the only product (eq 1). Triplet-sensitized photolysis under oxygen




(eq 1)

pressure (7 atm) afforded the quite labile endoperoxide **10b** (eq 1) as the only isolable peroxide. Unfortunately, under these irradiation conditions housane **3b** suffered decomposition to afford a complex peroxidic product mixture, which was not further characterized. Due to this instability of **3b**, the triplet lifetime of the biradical **2b** could not be determined by our dioxygen trapping method.[1h]

The photochemistry of azoalkane **1c** is similar to that of **1b**. Consequently, the bicyclopentane **3c** was obtained in the direct and benzophenone-sensitized photolyses in the absence of dioxygen. Under oxygen pressure the triplet-sensitized process afforded endoperoxide **10c**, which was reported previously.[12]

**Photoacoustic Measurements.** The lifetimes of the triplet biradicals **2a–c**, generated by benzophenone-sensitized photolysis of the azoalkanes **1a–c** in argon-purged acetonitrile, were determined by time-resolved photoacoustic calorimetry (PAC).[3,13] The signals were analyzed by convoluting the *T* wave with a triple exponential function corresponding to the three sequential reaction steps depicted in Figure 1.

The lifetime of the first process, i.e., formation of the thermally relaxed triplet state of benzophenone, is much shorter than the time resolution of our setup and was arbitrarily fixed at $\tau_1 = 1$ ns; its heat release $\Delta H_1$ was fixed at 46.2 and 23.8 kcal mol$^{-1}$ for 248- and 308-nm excitation,

(6) (a) Gassman, P. G.; Mansfield, K. T. *Org. Synth.* **1969**, *49*, 1. (b) Adam, W.; De Lucchi, O. *Angew. Chem.* **1980**, *92*, 815; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 762.

(7) Corey, E.; Narasaka, K.; Shibasaki, M. *J. Am. Chem. Soc.* **1976**, *98*, 6417.

(8) (a) Thiele, J. *Chem. Ber.* **1901**, *34*, 68. (b) Franklin, W. E.; Mack, H.; Rowland, S. P. *J. Org. Chem.* **1968**, *33*, 626.

(9) Wahren, R. *J. Organomet. Chem.* **1973**, *57*, 415.

(10) Riemenschneider, R.; Nerin, R. *Monatsh. Chem.* **1960**, *91*, 829.

(11) Baldwin, J. E.; Andrews, G. P. *J. Org. Chem.* **1988**, *53*, 4624.

(12) Adam, W.; Grabowski, S.; Platsch, H.; Hannemann, K.; Wirz, J. *J. Am. Chem. Soc.* **1989**, *111*, 751.

(13) Melton, L. A.; Ni, T.; Lu, Q. *Rev. Sci. Instrum.* **1989**, *60*, 3217.

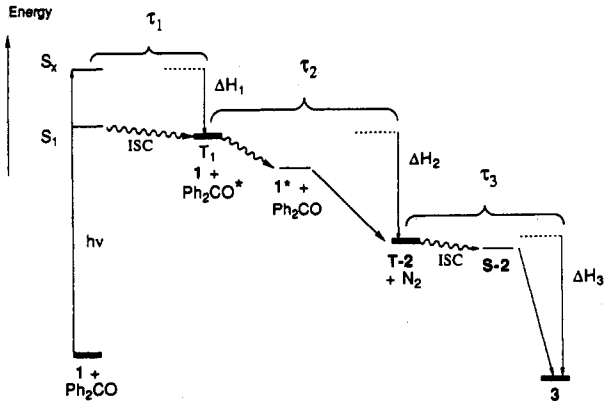



**Figure 1.** Energy scheme of the benzophenone-sensitized photolysis.

based on the known value of the triplet energy of benzophenone (69.0 kcal mol$^{-1}$).[14]

The second process includes both energy transfer from triplet benzophenone to the azoalkanes 1 and nitrogen extrusion from the excited azoalkanes to yield the triplet biradicals **2**. Its lifetimes $\tau_2$, which depended on the concentration of the azoalkanes, agreed within the error limits with those determined on the same solutions by monitoring the transient absorbance of triplet benzophenone at 530 nm.

To determine the lifetime of the third process $\tau_3$ (decay of the triplet biradicals **2**), the concentration of the azoalkanes was chosen at about $2.5 \times 10^{-2}$ M, which gave $\tau_3$ values over 25 times longer than the $\tau_2$ lifetimes (ca. 10 ns). Eight normalized traces were averaged for each measurement, and at least four independent measurements of both sample and reference were taken. The parameters obtained by the least-squares fitting procedure[13] and the standard errors of the sample means are listed in Table I, together with triplet lifetimes determined previously by different methods. Note that the absolute errors of the calorimetric values $\Delta H_2$ and $\Delta H_3$ may well be much larger than the quoted reproducibilities. The quantum yields of nitrogen extrusion from the triplet excited azoalkanes were *assumed* to be unity, based on the unity value reported for **1a**.[15] The effects of volume change were *not* considered. Nevertheless, these simplifications do not affect the values of the triplet biradical lifetimes reported presently, which are of prime interest here.

## Discussion

Our triplet lifetime value of 258 ± 14 ns for the parent 1,3-cyclopentadiyl **2a** (Table I, entry 1) is in rather good agreement with the reported PAC value,[3c] namely 316 ± 80 ns in benzene.[16] In the latter work the PAC curves were convoluted only by means of a double-exponential process. Therefore, in our triple-exponential convolution it was not necessary to accelerate the energy transfer from the excited benzophenone to the azoalkane **1a** by operating at high concentrations of **1a**. Furthermore, we confirmed the lifetime of the excited benzophenone determined by PAC ($\tau_2$ = 15 ± 3 ns, Table I) independently through time-resolved laser flash photolysis ($\tau_2$ = 13 ± 2 ns) under

**Table I. PAC Parameters[a] and Triplet Lifetimes of 1,3-Cyclopentanediyl Biradicals**

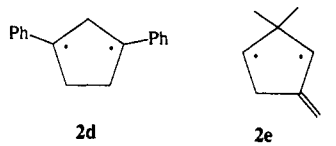
| biradical | $\Delta H_2$ (kcal/mol) | $\tau_2$ (ns) | $\Delta H_3$ (kcal/mol) | $\tau_3$ (ns) present | $\tau_3$ (ns) previous |
|---|---|---|---|---|---|
| **2a**[b] | 58.9 ± 1.4 | 15 ± 3 | 55.2 ± 2.3 | 258 ± 14 | ~100[c] |
| | | | | | 316 ± 80[d] |
| **2b**[e] | 73.4 ± 0.9 | 9 ± 2 | 26.8 ± 4.3 | 281 ± 36 | *f* |
| **2c**[e] | 71.6 ± 0.7 | 3 ± 2 | 27.4 ± 1.1 | 334 ± 8 | 380 ± 30[g] |

[a] In $CH_3CN$, errors given are the standard deviation of at least four experiments. [b] Excitation wavelength λ = 248 nm. [c] Determined by oxygen trapping, see ref 1h. [d] Determined by PAC, see ref 3c. [e] Excitation wavelength λ = 308 nm. [f] Not reported. [g] Determined by time-resolved laser flash photolysis, see ref 12.

identical conditions. Still more gratifying are our results for the phenyl-substituted biradical **2c**, for which the triplet lifetime measured by the PAC experiment ($\tau_3$ = 334 ± 8 ns, Table I, entry 3) matches well the previously determined value by time-resolved laser flash spectroscopy ($\tau_3$ = 380 ± 30 ns).[12]

This excellent correspondence reflects a high degree of confidence in the triplet biradical lifetimes obtained by the PAC method. Yet, it should be pointed out that the PAC values for the triplet lifetime of biradical **2a** are significantly higher (ca. 3-fold) than estimated by the oxygen trapping method ($\tau_3 \sim$ 100 ns). This presumably arises from the fact that too low a value for the unknown rate constant of oxgen trapping ($k_{O_2}$) was used to estimate the lifetime from the competition kinetics in the oxygen trapping.[1h] By taking the value for the rate constant $k_{O_2}$ = $5.3 \times 10^9$ M$^{-1}$ s$^{-1}$, determined directly from PAC experiments,[3c] the oxygen trapping technique leads to a triplet lifetime for **2a** of 351 ± 57 ns, which is in excellent accord with the present and previous[3c] PAC results.

More significant, comparison of the triplet lifetimes of the biradicals **2** show that neither allylic conjugation as in biradical **2b** nor benzylic conjugation as in **2c** cause a pronounced prolongation of the lifetimes relative to the parent 1,3-cyclopentadiyl **2a**. This is rather astounding, especially if one recalls that 1,3 diphenyl substitution[17] causes a massive increase (ca. 100-fold) of the triplet lifetime for **2d** in acetonitrile ($\tau_3$ = 16 000 ± 2000 ns).[18]




**2d** **2e**

For the latter, three factors[1h,18] were proposed to be responsible for its long triplet lifetime: (a) delocalization at the radical centers, which diminishes spin density and thus a decrease in the overlap necessary for effective intersystem crossing by spin orbit coupling (SOC),[19] (b) rigidity by conjugation, which inhibits pyrimidalization at the radical centers and thus reduction of SOC, and (c) stabilization of the biradical thermodynamically relative to its housane product, which imparts kinetic persistence. If conjugation (point a) were to play the dominant role in

(14) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin Cummings: Menlo Park, CA, 1978.
(15) Clark, W. D. K.; Steel, C. *J. Am. Chem. Soc.* **1971**, *93*, 6347.
(16) For the gas-phase triplet lifetime of **2a** (195 ns) determined by CARS see ref 1j.
(17) (a) The 4,5-dimethylene-1,3-cyclopentanediyl diradical (see refs 17b and 4a) constitutes a non-Kekulé system and is thus different from **2b**. (b) Roth, W. R.; Kowalczik, U.; Maier, G.; Reisenauer, H. P.; Sustmann, R.; Müller, W. *Angew. Chem.* **1987**, *99*, 1330; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1283.
(18) Adam, W.; Wirz, J.; Reinhard, G.; Platsch, H. *J. Am. Chem. Soc.* **1990**, *112*, 4570.
(19) Salem, L.; Rowland, C. *Angew. Chem.* **1972**, *84*, 86; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

enhancing the triplet lifetimes of the 1,3-cyclopentadiyls **2**, a more pronounced increase would have been expected in the order **2a** < **2c** < **2b**; i.e., allylic conjugation[20] should be most effective. In regard to point c, the heats of reaction of the cyclization of the triplet biradicals **2** to their bicyclopentanes **3**, determined by the PAC experiment ($\Delta H_3$ in Table I), imply that significant thermodynamic stabilization during housane formation is obtained also for the biradicals **2b** and **2c**. Consequently, our present data suggest that the prominent factor, which causes the extraordinary enhancement of the triplet lifetime of biradical **2d**, is the increase in rigidity (point b). This implies that the flexibility of the one remaining unconjugated radical center allows sufficient pyramidalization to achieve the favorable orbital orientation required in the SOC process[18,19] and hence increased intersystem crossing to the singlet biradical and subsequent cyclization to the housane product **3**. Such pyramidalization is in accord with the experimental results for the allyl-conjugated biradical **2b**,[5b] from which an activation barrier for ISC was concluded.

Finally, with the triplet lifetime of biradical **2b** made available, it is now possible to assess the effect of *gem*-dimethyl substitution in the biradical **2e**. In view of the low yield of oxygen trapping products,[2a] the triplet lifetime of the latter was estimated to be at best a few nanoseconds. Thus, a ca. 200-fold decrease of the triplet lifetime results for **2e** by introducing *gem*-dimethyl substituents in **2b**. A similar diminution of the triplet lifetime due to *gem*-dimethyl substitution was also observed for the biradicals **2a,d**, whose 2,2-dimethyl derivatives show significantly shorter lifetimes than their corresponding parent systems.[2a,18] This was rationalized by changes in the singlet–triplet energy gap[2a,21] as a result of perturbation of "through-bond" coupling.

In conclusion, allyl or benzyl conjugation at a single radical site in 1,3-cyclopentanediyl biradicals changes only nominally their triplet lifetimes. Presumably sufficient flexibility remains in the biradical skeleton to permit efficient intersystem crossing through pyramidalization despite the conjugation. Furthermore, *gem*-dimethyl substitution reduces drastically the triplet lifetime in such biradicals, apparently a general phenomenon, which derives from changes in the singlet–triplet energy gap.

## Experimental Section

**General Aspects.** Gas chromatography analyses were conducted on a capillary GC instrument, equipped with a flame ionization detector (FID). For the analysis of 2-methylenebicyclo-[2.1.0]pentane (**3b**) a 30-m OV-1 fused silica column was used with injector, column, and detector temperatures of 125, 20, and 150 °C ($N_2$: 0.7 kp/cm$^2$). IR data are given in cm$^{-1}$.

A Coherent Innova 100 argon ion laser, fitted with a selected UV tube, was used as irradiation source. All irradiations were conducted in Griffin–Worden tubes as previously described.[22] For the time-resolved photoacoustic calorimetry (PAC) a Lambda Physik EMG 101 MSC excimer laser was used.

**Preparation of the Azoalkanes.** Solvents and commercially available chemicals were purified by standard procedures. Column chromatography was carried out on silica gel (0.032–0.063 μm, Woelm).

**2,3-Diazabicyclo[2.2.1]hept-2-ene (1a)** was prepared according to the known procedure.[6a]

**1-(Methoxycarbonyl)-4-methyl-2,4,6-triazatricyclo[5.2.1.0$^{2,6}$]-dec-8-ene-3,5-dione (4b′).** The dimeric methylcyclopentadiene carboxylate (Thiele's ester,[8] 5.30 g, 21.3 mmol) was cracked by distillation at 160 °C/0.1 Torr into its monomer, which was collected in a receiver at −78 °C. The monomeric ester was dissolved in 15 mL of dichloromethane, and 4-methyl-1,2,4-triazoline-3,5-dione[23] (3.42 g, 3.07 mmol) was added at −20 °C in small portions until the red color remained. The solvent was evaporated at 25 °C/15 Torr, and the solid residue was recrystallized from methanol, which gave colorless needles, 6.20g (86%), mp 122–124 °C dec: IR (KBr) 3100, 3075, 2995, 2980, 1780, 1745, 1720, 1555, 1445, 1400; $^1$H NMR (250 MHz, $CDCl_3$) δ 2.10 (dd, $J$ = 8.7, 1.5 Hz, 1 H, $CH_2$), 2.45 (dd, $J$ = 8.7, 1.6 Hz, 1 H, $CH_2$), 2.89 (s, 3 H, $NCH_3$), 3.86 (s, 3 H, $OCH_3$), 5.05 (dq, $J$ = 2.3, 1.5 Hz, 1 H, CH), 6.32 (dd, $J$ = 5.5, 2.3 Hz, 1 H, H-C=), 6.50 (dd, $J$ = 5.5, 1.5 Hz, 1 H, CH); $^{13}$C NMR (63 MHz, $CDCl_3$) δ 25.7 (q, $NCH_3$), 53.3 (q, $OCH_3$), 53.7 (t), 65.2 (d), 76.0 (s), 131.1 (d, HC=), 131.8 (d, HC=), 159.6 (s, C=O), 159.8 (s, C=O), 166.7 (s, $CO_2$); MS (70 eV) $m/z$ 237 (16) [M$^+$], 205 (92), 180 (24), 148 (25), 124 (100), 96 (46), 93 (51), 65 (40). Anal. Calcd for $C_{10}H_{11}N_3O_4$: C, 50.63; H, 4.68; N, 17.71. Found: C, 50.88; H, 4.70; N, 17.54.

**8-(Methoxycarbonyl)-4-methyl-2,4,6-triazatricyclo[5.2.1.0$^{2,6}$]-dec-8-ene-3,5-dione (4b).** The urazole **4b′** (18.4 g, 77.7 mmol) was refluxed in 215 mL of chlorobenzene under a nitrogen gas atmosphere for 3h.[7] After removal of the solvent at 25 °C/0.1 Torr, 15 mL of MeOH was added to the liquid residue. When the residue was cooled in an ice bath, colorless needles separated, which were collected and dried under vacuum, 13.4 g (72%), mp 104–106 °C: IR (KBr) 3090, 2960, 1790, 1745, 1710, 1595, 1450, 1400, 1290, 1190; $^1$H NMR (250 MHz, $CDCl_3$) δ 1.99 (dt, $J$ = 9.4, 1.4 Hz, 1 H, $CH_2$), 2.22 (dtd, $J$ = 9.4, 1.5, 1.1 Hz, 1 H, $CH_2$), 2.86 (s, 3 H, $NCH_3$), 3.74 (s, 3 H, $OCH_3$), 5.10 (q, $J$ = 1.4 Hz, 1 H, CH), 5.29 (t, $J$ = 1.5 Hz, 1 H, CH), 6.91 (t, $J$ = 1.4 Hz, 1 H, HC=); $^{13}$C NMR (63 MHz $CDCl_3$) δ 25.8 (q, $NCH_3$), 49.0 (t), 52.4 (q, $OCH_3$), 63.8 (d), 64.2 (d), 136.5 (s), 136.9 (d), 158.9 (s, C=O), 159.5 (s, C=O), 162.4 (s, $CO_2$); MS (70 eV) $m/z$ 237 (20) [M$^+$], 205 (100), 180 (17), 148 (31), 124 (83), 96 (40), 93 (52), 79 (39). Anal. Calcd for $C_{10}H_{11}N_3O_4$: C, 50.63; H, 4.68; N, 17.71. Found: C, 50.79; H, 4.79; N, 17.41.

**8-*endo*-(Methoxycarbonyl)-4-methyl-2,4,6-triazatricyclo-[5.2.1.0$^{2,6}$]decane-3,5-dione (5b).** A solution of the urazole **4b** (8.30 g, 34.9 mmol) in 120 mL of ethyl acetate was hydrogenated at 1 atm over 10% Pd/C (100 mg) for 14 h at room temperature. The catalyst was removed by filtration and the solvent evaporated at 25 °C/15 Torr. The crude product was recrystallized from ethanol to yield colorless plates, 7.71 g (92%), mp 87–88 °C: IR (KBr) 2975, 1760, 1720, 1700, 1450, 1390, 1355, 1320, 1290, 1260; $^1$H NMR (250 MHz, $CDCl_3$) δ 1.72–1.85 (m, 2 H, $CH_2$), 2.00 (ddd, $J$ = 13.6, 11.3, 3.3 Hz, 1 H, $CH_2$), 2.48 (ddd, $J$ = 13.6, 4.4, 2.5 Hz, 1 H, $CH_2$), 3.01 (s, 3 H, $NCH_3$), 3.06 (ddd, $J$ = 11.3, 4.4, 3.6 Hz, 1 H, CH), 3.77 (s, 3 H, $OCH_3$), 4.62 (s, 1 H, CH), 4.84 (s, 1 H, CH); $^{13}$C NMR (63 MHz, $CDCl_3$) δ 25.6 (q, $NCH_3$), 30.6 (t), 39.2 (t), 45.4 (d), 52.5 (q, $OCH_3$), 60.3 (d), 62.6 (d), 158.9 (s, C=O), 159.1 (s, C=O), 171.2 (s, $CO_2$); MS (70 eV) $m/z$ 239 (75) [M$^+$], 208 (33), 207 (14), 180 (17), 179 (12), 165 (15), 153 (100), 152 (81). Anal. Calcd for $C_{10}H_{13}N_3O_4$: C, 50.21; H, 5.48; N, 17.56. Found: C, 50.63; H, 5.36; N, 17.13.

**8-*endo*-(Hydroxymethyl)-4-methyl-2,4,6-triazatricyclo-[5.2.1.0$^{2,6}$]decane-3,5-dione (6b).** $LiBH_4$ (2.40 g, 110 mmol) and *B*-methoxy-9-borabicyclo[3.3.1]nonane[4,24] (B-MeO-9-BBN, 855 mg, 5.62 mmol) were added to ester **5b** (12.8 g, 53.7 mmol) in 100 mL of dry THF under argon gas atmosphere at 0 °C. After being stirred for 14 h at room temperature, the reaction mixture was hydrolyzed with 25 mL of an aqueous solution of $NH_4Cl$ and

(20) (a) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1988**, 31. (b) Merenyi, R. Janousek, Z.; Viehe, H. G. In *Substituent Effects in Radical Chemistry*; Viehe, H. G., Ed.; Reidel: Dordrecht, Netherlands, 1986; p 301.

(21) (a) Doubleday, C., Jr.; McIver, J. W., Jr.; Page, M. *J. Am. Chem. Soc.* **1982**, *104*, 6533. (b) Goldberg, A. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 284.

(22) (a) Adam, W.; Hannemann, K.; Wilson, R. M. *J. Am. Chem. Soc.* **1980**, *108*, 928. (b) Wilson, R. M.; Wunderly, S. W.; Walsh, T. F.; Musser, A. K.; Outcalt, R.; Geiser, F.; Gee, S. K.; Brabender, W.; Yerino, L.; Conrad, T. T.; Tharp, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 4429 and references cited therein.

(23) Strickler, J. C.; Pivkle, W. P. *J. Org. Chem.* **1966**, *31*, 3444.

(24) Brown, H. C.; Negiski, E.; Bake, P. L. *J. Am. Chem. Soc.* **1972**, *94*, 3561.

most of the organic solvent was distilled off at 25 °C/15 Torr. The residue was extracted with dichloromethane (12 × 30 mL), and the combined organic layers were dried over anhydrous sodium sulfate and evaporated at 25 °C/15 Torr. On column chromatography (15:1 ethyl acetate/methanol as eluent) of the crude product, the alcohol **6b** was obtained as a colorless oil, 8.93 g (78%): IR (film) 3470, 2960, 2880, 1775, 1710, 1460, 1400, 1205, 1110, 1050; $^1$H NMR (250 MHz, $CDCl_3$) δ 1.24 (ddd, $J$ = 13.2, 4.8, 2.4 Hz, 1 H, $CH_2$), 1.46 (dm, $J$ = 11.0 Hz, 1 H, $CH_2$), 1.66 (br d, $J$ = 11.0 Hz, 1 H, $CH_2$), 1.87 (ddd, $J$ = 13.2, 11.3, 3.4 Hz, 1 H, $CH_2$), 2.20–2.36 (m, 1 H, CH), 2.90 (s, 3 H, $NCH_3$), 3.51–3.65 (m, 2 H, $CH_2O$), 3.98 (s, 3 H, $OCH_3$), 4.42 (br s, 1 H, CH), 4.56 (br s, 1 H, CH); $^{13}$C NMR (63 MHz, $CDCl_3$) δ 25.5 (q, $NCH_3$), 29.3 (t), 38.4 (t), 42.3 (d), 60.5 (d), 61.6 (d), 61.8 (t), 159.1 (s, C=O), 160.3 (s, C=O); MS (70 eV) $m/z$ 211 (60) [M$^+$], 152 (47), 116 (50), 115 (59), 97 (33), 96 (43), 79 (100), 76 (68). Anal. Calcd for $C_9H_{13}N_3O_3$: C, 51.18; H, 6.20; N, 19.89. Found: C, 51.63; H, 6.25; N, 19.89.

**8-*endo*-[[(Methanesulfonyl)oxy]methyl]-4-methyl-2,4,6-triazatricyclo[5.2.1.0$^{2,6}$]decane-3,5-dione (7b).** To a solution of urazole **6b** (7.90 g, 37.4 mmol) in 150 mL of dichloromethane were added dry triethylamine (7.70 g, 76.2 mmol) and methanesulfonyl chloride (12.5 g, 109 mmol) under an argon gas atmosphere at 0 °C. The reaction mixture was stirred for 20 h at room temperature and hydrolyzed with 40 mL of aqueous $NH_4Cl$. The product was extracted with dichloromethane (3 × 60 mL), and the combined organic layers were washed with aqueous NaCl (1 × 50 mL). Upon drying over anhydrous sodium sulfate, the solvent was removed at 25 °C/15 Torr. The crude product was recrystallized from ethyl acetate to give colorless needles, 8.87 g (82%): mp 119–120 °C; IR (KBr) 3030, 2960, 1770, 1720, 1455, 1400, 1350, 1280, 1210, 1190; $^1$H NMR (250 MHz, $CDCl_3$) δ 1.38 (ddd, $J$ = 13.4, 4.7, 2.6 Hz, 1 H, $CH_2$), 1.53–1.71 (m, 2 H, $CH_2$), 1.97 (ddd, $J$ = 13.4, 11.2, 3.4 Hz, 1 H, $CH_2$), 2.46–2.60 (m, 1 H, $CH_2$), 2.95 (s, 3 H, $NCH_3$), 2.99 (s, 3 H, $SCH_3$), 4.17–4.30 (m, 2 H, $CH_2O$), 4.50 (br s, 1 H, CH), 4.56 (br s, 1 H, CH); $^{13}$C NMR (63 MHz, $CDCl_3$) δ 25.6 (q, $NCH_3$) 31.2 (t), 37.2 (q, $SCH_3$), 37.8 (t), 39.0 (d), 60.4 (d) 61.2 (d), 69.0 (t), 159.6 (s, C=O), 160.2 (s, C=O); MS (70 eV) $m/z$ 289 (23) [M$^+$], 210 (5), 194 (18), 152 (43), 115 (20), 80 (26), 79 (100), 69 (59). Anal. Calcd for $C_{10}H_{15}N_3O_5S$: C, 41.51; H, 5.22; N, 14.52. Found: C, 41.83; H, 5.07; N, 14.57.

**8-Methylene-4-methyl-2,4,6-triazatricyclo[5.2.1.0$^{2,6}$]decane-3,5-dione (8b).** A few drops of dry methanol (ca. 50 μL) were added to mesylate **7b** (1.99 g, 6.88 mmol) and potassium hydride (1.25 g, 23.1 mmol) in 200 mL of dry THF under an argon gas atmosphere. After being refluxed for 20 h, the reaction mixture was cooled in an ice bath and filtered under an argon gas atmosphere. The clear filtrate was concentrated at 25 °C/15 Torr and submitted to chromatography with ethyl acetate as eluent. Urazole **8b** was obtained as colorless needles, 438 mg (33%), mp 97–98 °C: IR (KBr) 3040, 1775, 1720, 1460, 1400, 1275, 1225, 1105, 1040, 1005; $^1$H NMR (250 MHz, $CDCl_3$) δ 1.88 (dt, $J$ = 10.5, 1.5 Hz, 1 H, $CH_2$), 2.19 (ddt, $J$ = 10.5, 1.5, 1.4 Hz, 1 H, $CH_2$), 2.30–2.35 (m, 2 H, $CH_2$), 2.91 (s, 3 H, $NCH_3$), 4.51 (br s, 1 H, CH), 4.58 (br s, 1 H, CH), 4.87 (t, $J$ = 1.5 Hz, 1 H, $H_2C$=), 5.18 (t, $J$ = 1.5 Hz, 1 H, $H_2C$=); $^{13}$C NMR (63 MHz, $CDCl_3$) δ 25.5 (q, $NCH_3$), 34.7 (t), 40.0 (t), 59.4 (d), 64.1 (d), 110.6 (t, $H_2C$=), 141.3 (s, C=), 157.3 (s, C=O), 158.0 (s, C=O); MS (70 eV) $m/z$ 193 (15) [M$^+$], 115 (7), 80 (16), 79 (100), 78 (10), 77 (15), 41 (4), 49 (7). Anal. Calcd for $C_9H_{11}N_3O_2$: C, 55.96; H, 5.74; N, 21.75. Found: C, 56.39; H, 5.87; N, 21.63.

**5-Methylene-2,3-diazabicyclo[2.2.1]hept-2-ene (1b).**[4] Urazole **8b** (720 mg, 3.73 mmol) and potassium hydroxide (2.07 g, 37.0 mmol) were suspended in 50 mL of isopropyl alcohol and refluxed for 14 h under a nitrogen gas atmosphere. The reaction mixture was poured on 120 mL of ice–water, and the aqueous solution was acidified with trifluoroacetic acid until pH 3. Upon stirring for 15 min, the reaction mixture was adjusted to pH 5 with aqueous ammonia, and 5 mL of a saturated, aqueous solution of $CuCl_2$ was added. The red precipitate was collected by filtration, washed with 5 mL of distilled water, and dissolved in 250 mL of aqueous ammonia. The blue solution was extracted with dichloromethane (5 × 60 mL), and the combined organic layers were washed with distilled water (2 × 50 mL) and with aqueous NaCl (2 × 50 mL) and dried over sodium sulfate. After evaporation of the solvent at 0 °C/15 Torr, distillation of the residue at −10 °C/0.1 Torr yielded a colorless liquid, 348 mg (86%): IR ($CCl_4$) 3120, 3060, 3020, 2990, 2960, 1680, 1505, 1450, 1440, 1200; UV (*n*-pentane) λ (ε) 347 nm (225), 364 nm (2); $^1$H NMR (200 MHz, −20 °C, $CDCl_3$) δ 1.46 (d, $J$ = 10.2 Hz, 1 H, $CH_2$), 1.49 (dq, $J$ = 10.2, 2.0 Hz, 1 H, $CH_2$), 1.68 (dm, $J$ = 16.2 Hz, 1 H, $CH_2$), 2.16 (dq, $J$ = 16.2, 2.0 Hz, 1 H, $CH_2$), 4.95 (t, $J$ = 2.0 Hz, 1 H, $H_2C$=), 5.28–5.30 (m, 2 H, $H_2C$= und CH), 5.40 (br s, 1 H, CH); $^{13}$C NMR (50 MHz, $CDCl_3$) δ 28.2 (t), 42.5 (t), 77.5 (d), 84.4 (d), 110.5 (t, $H_2C$=), 140.2 (s, C=); MS (70 eV) $m/z$ 80 (46) [M$^+$ − $N_2$], 79 (100), 77 (35), 53 (9), 52 (16), 51 (15), 50 (11), 41 (12).

**1,4- and 1,8-Diphenyl-2,4,6-triazatricyclo[5.2.1.0$^{2,6}$]dec-8-ene-3,5-diones (8c,c').** 1-Phenyl-2-cyclopent-1-ol[10] (7.30 g, 45.7 mmol) was dissolved in 100 mL of $CHCl_3$, which contained one drop of concentrated hydrochloric acid. Upon being stirred for 90 min at 20 °C, the reaction mixture was quenched by adding anhydrous potassium carbonate. After filtration and cooling to 0 °C, *N*-phenyl-1,2,4-triazoline-3,5-dione was added until its red color remained (5.64 g, 32.1 mmol). The reaction mixture was stirred for 1 h at 0 °C and directly subjected to the diimide hydrogenation procedure given below. Purification of the crude product was not possible due to facile retrocyclization: $^1$H NMR (60 MHz, $CDCl_3$) δ 1.7–2.5 (m, aliph H), 5.0 (br s, bridgehead H), 5.3 (br s, bridgehead H), 6.2–6.8 (m, HC=), 7.0–7.7 (m, arom H).

**1,4- and 1,8-Diphenyl-2,4,6-triazatricyclo[5.2.1.0$^{2,6}$]decane-3,5-dione (9c,c').** Potassium azodicarboxylate[25] (49.9 g, 257 mmol), which should be handled with caution for its potential to detonate, especially when impure, was added to a mixture of the isomers **8c,c'** (10.2 g, 32.1 mmol) in 100 mL of $CHCl_3$ at 0 °C under a nitrogen gas atmosphere. Glacial acetic acid (30.8 g, 514 mmol) in 30 mL of $CHCl_3$ was administered dropwise over a period of 4 h to the efficiently stirred solution at 0 °C. After the mixture was stirred for an additional 10 h at room temperature, the yellow solid was removed by filtration and the solvent was evaporated at 20 °C/15 Torr. The residue was recrystallized from methanol to yield a mixture of the two isomers **9c,c'**, which was separated by silica gel chromatography with petroleum ether/ethyl acetate (3:2) as eluent. The two isomers were obtained as colorless needles, 5.63 g (55%), mp 158–159 °C for **9c** and 199–200 °C for **9c'**. It proved to be more practical to convert the isomeric mixture **9c,c'** first to the azoalkanes **1c,c'** before chromatographic separation (see below). Isomer **9c**: IR (KBr) 3060, 2950, 1710, 1495, 1400, 1171, 1145, 1057, 743, 692; $^1$H NMR (400 MHz, $CDCl_3$) δ 2.08 (m, 2 H, $CH_2$), 2.17 (m, 1 H, $CH_2$), 2.39 (m, 2 H, $CH_2$), 2.64 (m, 1 H, $CH_2$), 7.29–7.62 (m, 10 H, arom H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 28.3 (t), 31.6 (t), 47.3 (t), 59.8 (d), 74.9 (s), 125.2 (d), 127.0 (d), 128.0 (d), 128.4 (d), 128.5 (d), 128.9 (d), 131.8 (s), 134.8 (s), 154.7 (s), 155.2 (s); MS (70 eV) $m/z$ 319 (2) [M$^+$], 143 (100), 142 (88), 128 (28), 119 (16), 91 (23), 77 (11). Isomer **9c'**: IR (KBr) 3060, 2970, 2940, 2900, 1705, 1500, 1400, 1133, 768, 740; $^1$H NMR (400 MHz, $CDCl_3$) δ 1.91 (d, $J$ = 2.0 Hz, 1 H, $CH_2$), 2.00 (m, 1 H, $CH_2$), 2.20 (m, 1 H, $CH_2$), 2.40 (dd, $J$ = 15.3, 13.2 Hz, 1 H, $CH_2$), 3.47 (m, 1 H, C*H*Ph), 4.80 (br s, 2 H, bridgehead H), 7.20–7.50 (m, 5 H, arom H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 35.0 (t), 39.7 (t), 45.0 (t), 61.7 (d), 65.1 (s), 125.3 (d), 127.0 (d), 128.2 (d), 128.4 (d), 129.1 (d), 131.6 (s), 138.9 (s), 157.9 (s), 158.2 (s); MS (70 eV) $m/z$ 319 (58) [M$^+$], 214 (100), 119 (40), 104 (85), 91 (54), 77 (11). Anal. Calcd for $C_{19}H_{17}N_3O_2$ (isomeric mixture): C, 71.46; H, 5.37; N, 13.16. Found: C, 71.14; H, 5.25; N, 13.27.

**1-Phenyl-2,3-diazabicyclo[2.2.1]hept-2-ene (1c).** The procedure for the conversion of **9c,c'** to **1c,c'** was identical to the preparation of azoalkane **1b** (see above). After column chromatography with petroleum ether/ethyl acetate (9:1) as eluent and recrystallization from petroleum ether/benzene, azoalkane **1c** was obtained as colorless needles, 206 mg (35%), mp 54.5–55.5 °C, and the isomer **1c'** as colorless plates, 217 mg (37%), mp 56–57 °C. Isomer **1c**: IR ($CCl_4$) 3065, 3038, 3018, 2985, 2950, 1615, 1602, 1495, 1445, 1332; UV (heptane) λ (ε) 345 (340), 340 (159); $^1$H NMR (200 MHz, $CDCl_3$) δ 1.14–1.39 (m, 2 H, $CH_2$), 1.44–1.63 (m, 2 H, $CH_2$), 1.72–1.92 (m, 2 H, $CH_2$), 5.30 (br s, 1 H, CH), 7.3–7.5 (m, 3 H, arom H), 7.6–7.7 (m, 2 H, arom H); $^{13}$C

(25) Berson, J. A.; Poonian, M. S.; Libbey, J. W. *J. Am. Chem. Soc.* **1969**, *91*, 5567.

NMR (50 MHz, $CDCl_3$) δ 23.0 (t), 27.8 (t), 44.6 (t), 77.9 (d), 89.6 (s), 126.8 (d), 127.7 (2 × d), 128.5 (2 × d), 138.2 (s); MS (70 eV) *m/z* 173 (1) [$M^+$ + 1], 144 (73), 143 (76), 129 (100), 128 (61), 115 (47), 77 (26), 66 (26), 51 (24). Anal. Calcd for $C_{11}H_{12}N_2$: C, 76.71; H, 7.02; N, 16.26. Found: C, 76.68; H, 7.24; N, 16.76. Isomer **1c'**: IR ($CCl_4$) 3010, 2955, 1600, 1495, 1448, 1250, 1231, 1123, 1031, 697; UV (heptane) λ (ε) 344 (275); $^1H$ NMR (200 MHz, $CDCl_3$) δ 1.18–1.35 (m, 1 H, $CH_2$), 1.35–1.46 (m, 2 H, $CH_2$), 2.15 (m, 1 H, $CH_2$), 3.25–3.40 (m, 1 H, C*H*Ph), 5.25 (br s, 1 H, CH), 5.45 (br s, 1 H, CH), 7.1–7.3 (m, 5 H, arom H); $^{13}C$ NMR (50 MHz, $CDCl_3$) δ 28.6 (t), 42.1 (d), 42.4 (t), 44.6 (t), 78.0 (d), 79.8 (d), 126.5 (d), 127.8 (2 × d), 128.2 (2 × d), 139.8 (s); MS (70 eV) *m/z* 172 (1) [$M^+$ + 1], 171 (0.4), 143 (58), 129 (100), 128 (52), 115 (35). Anal. Calcd for $C_{11}H_{12}N_2$: C, 76.71; H, 7.02; N, 16.26. Found: C, 76.94; H, 7.24; N, 16.54.

**Direct Photolysis of Azoalkane 1b.** In a sealed NMR tube, azoalkane **1b** (13.0 mg, 0.121 mmol) in $C_6D_6$ or toluene-$d_8$ was irradiated with all lines of the argon ion laser (UV output 1.5–1.6 W) for 3 min. By NMR and GC analysis 2-methylene-bicyclo-[2.1.0]pentane (**3b**)[11] was the only detected product (>99%): $^1H$ NMR (250 MHz, toluene-$d_8$) δ 0.68–0.75 (m, 2 H, $CH_2$), 1.68–1.74 (m, 1 H, CH), 1.84 (dt, *J* = 13.3, 1.8 Hz, 1 H, $CH_2$), 1.98–2.08 (m, 1 H, CH), 2.42 (dm, *J* = 13.3 Hz, 1 H, $CH_2$), 4.44–4.48 (m, 1 H, $H_2C$=), 4.70 (t, *J* = 1.8 Hz, $H_2C$=); $^{13}C$ NMR (50 MHz, $C_6D_6$) δ 14.0 (d), 19.4 (t), 25.3 (t), 33.3 (d), 101.3 (t), 147.9 (s).

**Sensitized Photolysis of Azoalkane 1b under Oxygen Gas Pressure.** A solution of the azoalkane **1b** (142 mg, 1.31 mmol) and benzophenone (250 mg, 1.37 mmol) in 15 mL of $CFCl_3$ in a Griffin–Worden tube was cooled to −25 °C under oxygen gas pressure (7 atm). The solution was allowed to equilibrate thermally for 30 min prior to irradiation with the 364-nm line of the argon ion laser (UV output 0.9–1.0 W). After irradiation for 4 h, removal of the solvent at 0 °C/15 Torr, and silica gel chromatography at −25 °C (3:1 dichloromethane/petroleum ether), 39 mg (27%) of the labile endoperoxide **11b** was obtained: IR ($CCl_4$) 3040, 3000, 3960, 1455, 1435, 1250, 1230, 1180, 1105, 1030; $^1H$ NMR (200 MHz, −20 °C, $CDCl_3$) δ 2.21 (d, *J* = 10.4 Hz, 1 H, $CH_2$), 2.30 (dq, *J* = 10.4, 2.2 Hz, 1 H, $CH_2$), 2.32 (dm, *J* = 16.9, 1 H, $CH_2$), 2.54 (dq, *J* = 16.9, 2.2 Hz, 1 H, $CH_2$), 4.87 (br s, 1 H, CH), 4.90 (br s, 1 H, CH), 4.93 (t, *J* = 2.2 Hz, 1 H, $H_2C$=), 5.19 (t, *J* = 2.2 Hz, 1 H, $H_2C$=); $^{13}C$ NMR (63 MHz, $CDCl_3$) δ 36.3 (t), 44.5 (t) 78.9 (d), 82.3 (d), 108.4 (t), 145.5 (s); MS (70 eV) *m/z* 112 (25) [$M^+$], 80 (8), 79 (100), 77 (17), 69 (6), 43 (25), 41 (28), 39 (39); calcd for $C_6H_8O_2$ 112.052, found 112.051 (MS).

**Sensitized Photolysis of Bicyclopentane 3b under Oxygen Gas Pressure.** Benzophenone-sensitized photolysis of housane **3b** in acetonitrile (0.018 M) under oxygen pressure (7 atm) as described above led to significant consumption of starting material within 20 min (monitored by GC). Thin-layer chromatography on silica gel with dichloromethane as eluent revealed at least one peroxide product (peroxide test spray[26]). Due to this instability of **3b**, the dioxygen trapping technique for determining the triplet lifetime of biradical **2b** could not be applied.

**General Procedure for the Photoacoustic Calorimetric Measurements.** The front face irradiation cell and the algorithm used for data analysis were those described by Melton, Caldwell, and co-workers.[3b,13] Excitation pulses from an excimer laser (248 or 308 nm, 25-ns pulse width) were attenuated to an energy of ca. 1 mJ per pulse. The cell thickness was fixed to 0.2 mm with a Teflon spacer. The signal of a 1-MHz contact transducer (Panametrics, A103) was fed into a 200-Ω input of the transient digitizer (Tektronix 7912 AD). A dielectric mirror (>99.9% reflection, 90° incidence angle) was placed in front of the transducer to reduce the background signal. 2-Hydroxybenzophenone in acetonitrile was used as a calibration standard for the system response (T-wave). The absorbances of the reference and sample solutions were adjusted to the same value around 0.7 to within 0.001 absorbance units in a 1-mm cell. In the sample solutions >96% of the absorbance was due to the sensitizer benzophenone; small corrections were applied where necessary to account for the fraction of light absorbed directly by the azoalkane. A flow cell was used to ensure exposure of fresh solutions to each excitation pulse. Each trace was normalized to correct for the minor shot-to-shot variations (±2%) in the excitation pulse energy using the digital output from a pyroelectric energy meter (Laser Precision Co., Rj-7620 energy meter, RjP-734 probe head).

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(26) Johnson, R. A.; Nidy, E. G. *J. Org. Chem.* **1975**, *40*, 1680.