the entering and leaving groups.[51] Most of these studies were in organic or aqueous organic solvents, and the high ionizing ability of water, even in a micelle, should lead to more open transition states with considerable ionic character.

Our observations are consistent with, but do not require, a mechanistic continuum from the carbonyl addition reactions in which nucleophilic attack by water, concerted with proton transfer, is rate limiting, to the S_N2-like mechanisms with concerted bond making and breaking, and then to the S_N1-like mechanisms in which bond breaking is the key step. In the S_N1-like mechanisms of the secondary alkyl halides, the rear of the substrate is exposed to water, but its interaction with the reaction center can best be regarded as solvation rather than as a covalent interaction.[23]

Micellar effects upon the rates of spontaneous hydrolyses have been cited as evidence for a porous-cluster micellar model,[9] and the absence of capture of the carbocation (or ion pair) by halide ion is consistent with this model. A diphenylmethyl substrate should penetrate deeply into the micelle, and if substrate ionization occurred in that region, the halide ion should be attracted by cationic head groups at the micellar surface, leaving the carbocation to be captured by water that had penetrated the micelle. Alternatively, one could suppose that the carbocation is not trapped by halide ion because its lifetime is so short that a water molecule reacts on encounter with it.[41a] However, in so far as the diphenylmethyl cation does discriminate between water and halide ion in aqueous acetone,[22] this explanation also requires the cation to be generated in a water-rich region of the micelle although, on the average, substrate may reside in an apolar region of the micellar core.

All our observations on the effects of micellar charge upon these spontaneous reactions can be fitted to the assumption that in addition to effects due to water activity in the micelle, there are those related to the apparent charge of the transition state. This apparent charge arises because the positive charge on an attacking water molecule can be dispersed into other water molecules and the negative charge of a leaving halide ion attracts hydrating water molecules (Schemes I and II). Therefore cationic and anionic micelles interact differently with the transition states for the various reactions, depending upon the importance of bond making and breaking, even though all the transition states are formally neutral. These micellar effects appear to be diagnostic of mechanism.

Acknowledgment. Support of this work by the National Science Foundation (Chemical Dynamics Program) is gratefullly acknowledged.

Registry No. $(PhO)_2CO$, 102-09-0; $(4\text{-}O_2NC_6H_4O)_2CO$, 5070-13-3; $(4\text{-}t\text{-}BuC_6H_4CO)_2O$, 22201-45-2; $(4\text{-}NCC_6H_4CO)_2O$, 16657-25-3; $(4\text{-}O_2NC_6H_4CO)_2O$, 902-47-6; $o\text{-}C_6H_4(CO)_2O$, 85-44-9; PhOCOCl, 1885-14-9; $4\text{-}O_2NC_6H_4OCOCl$, 7693-46-1; $PhSO_3Me$, 80-18-2; $PhCH_2Br$, 100-39-0; PhCHMeCl, 672-65-1; Ph_2CHCl, 90-99-3; Ph_2CHBr, 776-74-9; $(PhCO)_2O$, 93-97-0; PhCOCl, 98-88-4.

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(51) Shiner, V. J., Jr. In "Isotope Effects in Chemical Reactions"; Collins, C. J., Bowman, N. S., Eds.; Van Nostrand-Reinhold: Princeton, NJ, 1970; Chapter 2. Vitullo, V. P.; Grabowski, J.; Sridharan, S. *J. Chem. Soc. D* **1981**, 737.

Photochemistry of 1,1-Diazenes. Direct and Sensitized Photolyses of *N*-(2,2,5,5-Tetramethylpyrrolidyl)nitrene, *dl*-*N*-(2,5-Diethyl-2,5-dimethylpyrrolidyl)nitrene, and *N*-(2,2,6,6-Tetramethylpiperidyl)nitrene[1,2]

Peter G. Schultz[3] and Peter B. Dervan*[4]

Contribution No. 6594 from the Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125. *Received February 26, 1982*

Abstract: The photochemistry of the 1,1-diazenes *N*-(2,2,5,5-tetramethylpyrrolidyl)nitrene (**1**), *dl*-*N*-(2,5-diethyl-2,5-dimethylpyrrolidyl)nitrene (**2**), and *N*-(2,2,6,6-tetramethylpiperidyl)nitrene (**3**) is reported. The fluorescence spectrum of 1,1-diazene **1** has a 0–0 band at 607 nm, which is the maximum. The spacing between the peaks at 607 and 672 nm corresponds to the N═N stretch of S_0 consistent with the 1638-cm^{-1} stretch obtained from the infrared spectrum of **1**. The fluorescence quantum yields are $\phi_F = 2 \times 10^{-3}$ (MTHF, −78 °C), 7×10^{-3} (MTHF, −196 °C), and 1×10^{-3} (EPA, −196 °C). The fluorescence lifetime of **1** is $\tau_F = 2.3 \times 10^{-8}$ s ($CFCl_3$, −196 °C). Direct irradiation of **1** (466–610 nm, −78 °C) affords four hydrocarbon products, 54% **4**, 44% **5**, 2% **6 + 7** and tetrazene **8**. Triplet-sensitized photodecomposition afforded 74% **4**, 24% **5**, 2% **6 + 7** and tetrazene **8**. An approximate quantum yield for decomposition on direct irradiation is $\phi_D = 1.1 \times 10^{-2}$. From S_1, k_{N_2} is $>3.4 \times 10^5\ s^{-1}$, and reaction of S_0 with S_1, k_{DIM}, is $>4.2 \times 10^7$ L $mol^{-1}\ s^{-1}$ (at −78 °C). The spectrum of 1,1-diazene **2** reveals a structured absorption with λ_{max} 507 nm and a 0–0 band at 568 nm ($\epsilon = 20$). The vibrational spacing is 1270 cm^{-1}. The fluorescence spectrum of 1,1-diazene **2** has a 0–0 band at 620 nm, which is the maximum. The spacing between the maxima at 620 and 690 nm corresponds to the N═N stretch of S_0 consistent with the 1630-cm^{-1} stretch obtained for the infrared spectrum of **2**. The fluorescence quantum yield $\phi_F = 9 \times 10^{-3}$ (MTHF, −196 °C). The direct and sensitized irradiation of **2** in the visible affords hydrocarbon products **14–19** and tetrazene **20** in different ratios. The retention of stereochemistry in the cyclobutane products in the direct and sensitized photodecomposition was 98 and 68%, respectively, similar to the spin correlation effect seen in corresponding 1,2-diazene isomer. This indicates that for **2** (and by extension **1**) $k_{isc} << k_{N_2}$, consistent with a large S_1–T_1 gap in 1,1-diazenes. For 1,1-diazene **3** the fluorescence spectrum has a single maximum at 684 nm. The fluorescence quantum yield $\phi_F = 4 \times 10^{-4}$ (MTHF, −196 °C). The estimated fluorescence lifetime is $\tau_F = 4 \times 10^{-9}$ s. Direct irradiation of **3** in the visible at −78 °C afforded three hydrocarbon products, 29% **21**, 3% **22**, 68% **23** and tetrazene **25**.

The photochemistry of the 1,1-diazene (aminonitrene, *N*-nitrene) has not been examined due to this species transient nature.[5] Several theoretical groups have calculated the order of the electronic states of the 1,1-diazene during the past decade.[6]

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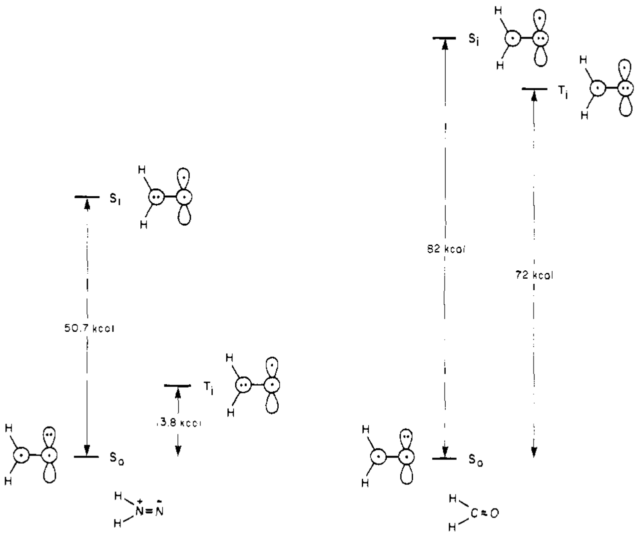
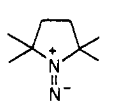
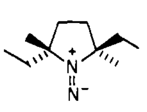
Goddard's GVB-CI calculations on the parent H_2N-N resulted in a ground-state singlet with low-lying n,π^* singlet (50.7 kcal) and triplet (13.8 kcal) states.[6f] These calculations reveal that the excited states of H_2N-N differ substantially from those of isoelectronic formaldehyde whose photochemistry has been well studied. For example, the S_1-T_1 energy gap is 37 kcal for H_2N-N and only 10 kcal for $H_2C=O$.[7] In addition, the bond strengths of 1,1-diazenes are much lower than those of carbonyl analogues.[8]



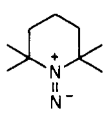
The recent synthesis and characterization of "persistent" 1,1-diazenes allow an investigation of the photochemical reactivity of these species.[2,8] We report here the photochemistry of three persistent 1,1-diazenes; *N*-(2,2,5,5-tetramethylpyrrolidyl)nitrene (**1**), *N*-(2,5-diethyl-2,5-dimethylpyrrolidyl)nitrene (**2**), and *N*-(2,2,6,6-tetramethylpiperidyl)nitrene (**3**). The infrared and electronic spectra and the kinetics of thermal decomposition of **1** and **3** have been previously documented.[8] 1,1-Diazene **2** has spectral and thermal behavior similar to that of **1**. Relevant to this photochemical study, 1,1-diazenes **1**–**3** absorb in the visible, revealing the low-lying S_1 (n,π^*) state (47–50 kcal), and are characterized by thermal reactions that occur with low energies of activation.[8] The E_a values for unimolecular loss of nitrogen from **1** and **3** are 17–20 kcal/mol depending on solvent.[8] The dimerization to tetrazene from **1** is slower than **3** by a factor of 90 at −41 °C, with E_a and log A values for the thermal dimerization of **3** being 6.4 kcal/mol and 3.8, respectively.[8d]



1



2



3

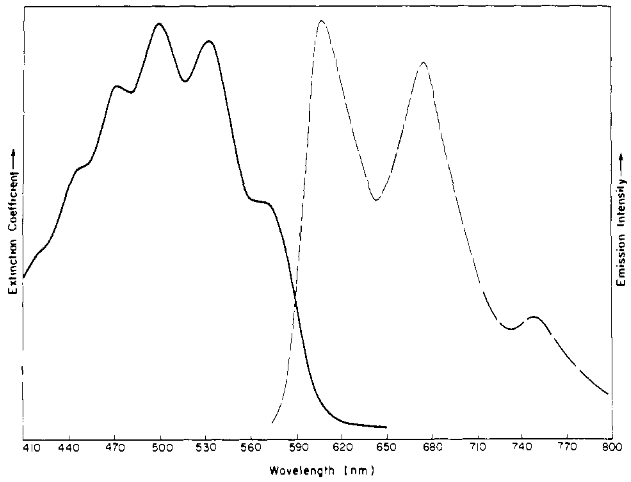


Figure 1. Absorption spectrum of **1** at −78 °C (—). Fluorescence spectrum of **1** at −196 °C (- - -).

Results and Discussion

***N*-(2,2,5,5-Tetramethylpyrrolidyl)nitrene (1).**[8] Addition of *tert*-butyl hypochlorite to a stirred solution of 1-amino-2,2,5,5-tetramethylpyrrolidine and triethylamine in anhydrous dimethyl ether at −78 °C affords, in addition to an insoluble white precipitate (Et_3NHCl), a red solution (λ_{max} 497 nm, $\epsilon = 20$, CH_2Cl_2) of the 1,1-diazene **1**, which is stable for days at −78 °C.[8] This solution is filtered at −78 °C, further purified by low-temperature chromatography (−85 °C) on basic alumina, and concentrated in $CFCl_3$. Low-temperature ^1H NMR spectroscopy (−60 °C, $CFCl_3$) reveals 98% 1,1-diazene **1**, 2% tetrazene **8**, and small amounts of dimethyl ether. When purified in this manner, **1** was shown to be stable at −78 °C in the absence of triethylamine,[9] a possible quencher of excited states.

The absorption and fluorescence spectra of 1,1-diazene **1** in $CFCl_3$ are shown in Figure 1. The absorption spectrum of **1** (λ_{max} 497 nm, 0–0 band 565 nm, $CFCl_3$)[10] is sufficiently resolved to give the vibrational spacing of S_1, 1238 cm^{-1} (N—N stretch). In CH_2Cl_2 1,1-diazene **1** has a λ_{max} of 497 nm and 0–0 band of 572 nm. The λ_{max} and 0–0 band both blue shift in 2-propanol to 487 and 552 nm, respectively. For the fluorescence spectrum the 0–0 band at 607 nm is the maximum.[10] The spacing between the peaks at 607 and 672 nm corresponds to the N=N stretch of S_0, consistent with the 1638-cm^{-1} stretch obtained from the infrared spectrum of **1**.[8] Warming **1** to 0 °C followed by recooling to −196 °C results in loss of the fluorescence signal. The absorption and fluorescence λ_{max} are separated by 100 nm, indicating that the equilibrium geometry of the S_0 and S_1 states of 1,1-diazene **1** differ substantially. The λ_{max} (0–0 band) of the fluorescence spectrum red shifts to 614 nm in more polar solvents (2-propanol). In both the absorption and fluorescence spectra the 0–0 bands and λ_{max} change with solvent polarity. This shift in 0–0 bands suggests that the thermally equilibrated ground and excited states must be differentially solvated, consistent with the differing degrees of electron delocalization in S_0 and S_1. In addition, the shapes of the absorption and corrected fluorescence spectra of **1** differ substantially.[11] Goddard calculates that S_0 is planar, whereas S_1 and T_1 have optimum pyramidal geometries. One possible explanation for the difference in absorption and fluorescence spectra is vibronic coupling in the pyramidal S_1 state.

The fluorescence rate constant k_F from S_1 (n,π^*) calculated from the integrated absorption spectra of **1** is 1.3×10^5 s^{-1}, typical of an n,π^* symmetry-forbidden transition.[12] The fluorescence

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(1) We are grateful to the National Science Foundation for generous support.

(2) For a preliminary report on part of this work, see: Schultz, P. G.; Dervan, P. B. *J. Am. Chem. Soc.* **1981**, *103*, 1563.

(3) National Science Foundation Predoctoral Fellow.

(4) Camille and Henry Dreyfus Teacher-Scholar, 1978–1983.

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(6) (a) Baird, N. C.; Barr, R. F. *Can. J. Chem.* **1973**, *51*, 3303. (b) Lathon, W. A.; Curtiss, L. A.; Hehre, W. J.; Lisle, J. B.; Pople, J. A. *Prog. Phys. Org. Chem.* **1974**, *11*, 1975. (c) Ahlrichs, R.; Staemmler, V. *Chem. Phys. Lett.* **1976**, *37*, 77. (d) Wagniere, G. *Theor. Chim. Acta.* **1973**, *31*, 269. (e) Baird, N. C.; Wernette, D. A. *Can. J. Chem.* **1977**, *55*, 330. (f) Davis, J. H.; Goddard, W. A. *J. Am. Chem. Soc.* **1977**, *99*, 7111.

(7) Gelbart, W. M. Elert, M. L., Heller, D. F. *Chem. Rev.* **1980**, *80*, 403.

(8) (a) Hinsberg, W. D., III; Dervan, P. B. *J. Am. Chem. Soc.* **1978**, *100*, 1608. (b) *Ibid.* **1979**, *101*, 6142. (c) Schultz, P. G.; Dervan, P. B. *Ibid.* **1980**, *102*, 878. (d) Hinsberg, W. D., III; Schultz, P. G.; Dervan, P. B. *Ibid.* **1982**, *104*, 766.

(9) 1,1-Diazenes decompose in the presence of trace acid.

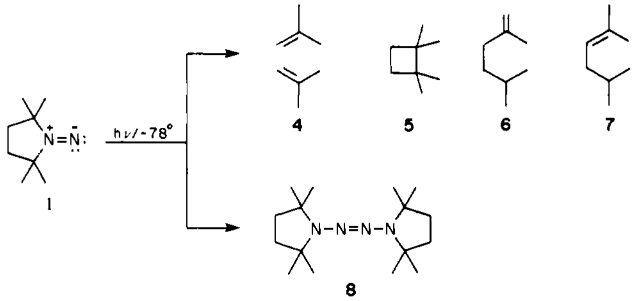
(10) If the bands assigned to the 0–0 transitions are in fact higher transitions, the 0–0 bands of the absorption and fluorescence spectra would exactly overlap, unlikely in light of the calculated dipole differences of 1.72 D between S_0 and S_1.[6f]

(11) The correction for instrument response is only 10% in the 600–700 nm range (see Experimental Section).

quantum yields (ϕ_F) determined relative to rubrene ($\phi_F = 1$)[13] are 2×10^{-3} (methyltetrahydrofuran (MTHF), −78 °C), 7×10^{-3} (MTHF, −196 °C), and 1×10^{-3} (EPA, −196 °C), indicating only modest sensitivity to temperature or solvent polarity. The fluorescence lifetime of **1**, $\tau_F = 2.3 \times 10^{-8}$ s ($CFCl_3$), was determined at −196 °C with a pulsed nitrogen dye laser.[14] Calculation of k_F (−196 °C) from $k_F = \phi_F/\tau_F$ affords a value for $k_F = 3 \times 10^5$ s^{-1}, not too different from the value calculated from the integrated absorption spectrum. τ_F was too short to be measured −78 °C. However, on the assumption that k_F is temperature insensitive, the calculated fluorescence lifetime of **1** at −78 °C is $\tau_F = 0.67 \times 10^{-8}$ s from $\phi_F/k_F = 2 \times 10^{-3}/3 \times 10^5$ s^{-1}.

Attempts to locate T_1 (n,π*) of **1** have to date been unsuccessful. No phosphorescence signals have been detected higher in energy than 26 kcal/mol (<1100 nm) on direct or sensitized irradiation, nor has an S_0–T_1 absorption been detected in the visible or near infrared with 1 M solutions of **1**.[15] Direct and sensitized irradiation of 1,1-diazene **1** in an ESR probe (at 78 and 10 K) failed to produce a triplet signal,[16] suggesting T_1 may be very short-lived. A strong signal from a doublet state grows in at 3300 G. Irradiation of solutions of tetrazene **8** under the same conditions affords the same doublet.

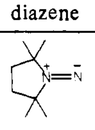
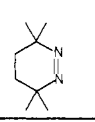
For photochemical studies, a degassed chromatographed solution of 1,1-diazene **1** (0.03 M in $CFCl_3$) was irradiated at 466–610 nm at −78 °C. After 12 h of irradiation at −78 °C the red color had completely disappeared. Vapor phase chromatography and ^1H NMR spectroscopy (−60 °C) revealed hydrocarbon products **4–7** and tetrazene **8** in a 1:4 ratio. The hydrocarbons **4–7** appear to be products from the photochemical extrusion of nitrogen from **1**. Tetrazene **8** probably results from the bimolecular reaction of S_1 and/or T_1 with S_0.



An approximate quantum yield for the decomposition of **1** on direct irradiation is $\phi_D{}^1 = 1.1 \times 10^{-2}$. The sum of the rates of loss of N_2 from S_1 (or vibrationally hot S_0) (k_{N_2}), reactions of S_1 with S_0 forming tetrazene (k_{DIM}), plus dimerization ($T_1 + S_0$) and loss of N_2 from T_1 ($\phi_D{}^3k_{isc}$) is equal to the overall decomposition rate $k_D = (\phi_D{}^3k_{isc} + k_{N_2} + k_{DIM}[S_0])$. Using the approximate quantum yield $\phi_D{}^1 = 1.1 \times 10^{-2}$ and the value $\tau_F = 0.67 \times 10^{-8}$ (−78 °C), we calculate from $k_D = \phi_D{}^1/\tau_F$ that $k_D = 1.6 \times 10^6$ s^{-1}. From the ratio of hydrocarbons/tetrazene products = 0.25 and initial concentration of S_0 (0.03 M), we calculate that $k_{N_2} < 0.008k_{DIM}$. As will be shown later for **2**, if $k_{isc} << (k_{N_2} + k_{DIM}[S_0])$, then from $k_D = k_{N_2} + k_{DIM}[S_0]$ one can calculate loss of N_2 from S_1, $k_{N_2} > 3.4 \times 10^5$ s^{-1}, and tetrazene formation from $S_1 + S_0$, $k_{DIM} > 4.2 \times 10^7$ L/(mol s).[18]

Triplet-sensitized photodecompositions were carried out at longer wavelengths at −78 °C. Irradiation of degassed chromatographed solutions of 1,1-diazene **1** (0.03 M in $CFCl_3$) at >608 nm in the presence of 0.02–0.05 M azulene sensitizer ($E_T = 31$ kcal)[19] affords hydrocarbons **4–7** and tetrazene **8** in a 1:9 ratio. Controls show that diazene **1** is unreactive upon direct irradiation at wavelengths >608 nm. The 1,2-diazene 3,3,6,6-tetramethyltetrahydropyridazine (**9**)[20] was not present (<0.5%) among the direct or sensitized decomposition products.

Table I. Hydrocarbon Products from 1,1- and 1,2-Diazenes 1 and 9

diazene	conditions	4	5	6 and 7
	0 °C, thermal[a]	47	49	4.0
	−10 °C, thermal[a]	53	44	3.0
	−20 °C, thermal[a]	59	39	2.0
	−78 °C, hν (direct)[a]	54	44	2.0
	−78 °C, hν (sens)[a,b]	74	24	2.0
	140 °C, thermal[c]	52	46	2.0
	−78 °C, hν (direct)[a]	56	42	2.0
	−78 °C, hν (sens)[d]	72	26	2.0

[a] $CFCl_3$. [b] Azulene. [c] Benzene. [d] CH_2Cl_2, thioxanthone.

For comparison the 1,2-diazene isomer **9** was photolyzed at >310 nm, yielding hydrocarbon products **4–7**. Sensitized photodecompositions in the presence of thioxanthone[21] also gave hydrocarbons **4–7**. The product compositions from the thermal, direct, and sensitized photodecomposition of 1,1-diazene **1** and the isomeric 1,2-diazene **9** are summarized in Table I.

The 2-methylpropene/tetramethylcyclobutane (**4**/**5**) ratios for direct and sensitized photodecomposition of 1,1-diazene **1** are 1.14 and 3.08, respectively. Importantly, the **4**/**5** product ratios are similar from the 1,1- and 1,2-diazene isomers in the direct and sensitized photolyses. Common singlet and triplet 1,4-biradicals (formed from loss of nitrogen from S_1 and T_1, respectively) from **1** and **9** would be sufficient to explain these results. Bartlett and Porter have shown a spin-correlation effect on the product ratios in the direct and triplet-sensitized photodecomposition of cyclic 1,2-diazenes similar to **9**.[22,23] Because the hydrocarbon product ratios from **1** are different for direct vs. sensitized photolyses, but in agreement with the product ratios from the 1,2-diazene isomer **9**, this may indicate a spin correlation effect in the 1,1-diazene case. This apparent lack of intersystem crossing would be consistent with the large calculated S_1–T_1 gap in the 1,1-diazene. To test explicitly whether $k_{isc} << k_{N_2}$ from S_1 of the 1,1-diazene, we have synthesized and studied the direct and sensitized photodecomposition of *N*-(2,5-diethyl-2,5-dimethylpyrrolidyl)nitrene (**2**). We will exploit the known behavior of highly substituted singlet and triplet biradicals (stereospecific vs. nonstereospecific) from the Bartlett–Porter study[22] as a *sensitive stereochemical test of the excited state precursor* to the hydrocarbon products from direct irradiation of 1,1-diazenes. If $k_{isc} > k_{N_2}$ from S_1, we might expect loss of stereochemical integrity in the closure products on direct irradiation. If $k_{isc} < k_{N_2}$ from S_1, we might expect a stereospecific result analogous to the 1,2-diazene results.

N-(2,5-Diethyl-2,5-dimethylpyrrolidyl)nitrene (2). A 2/1 mixture of the *dl* and *meso* isomers of 2,5-diethyl-2,5-dimethylpyrrolidine was synthesized in four steps from 2-nitrobutane[24] and methyl vinyl ketone. The *dl* amine hydrochloride **11** was isolated by fractional recrystallization from 2-propanol and identified by partial resolution of the hydrogen tartrate salt followed by conversion to the amine hydrochloride, $[\alpha]^{20}{}_{365}$ +4.80° (*c* 0.39, methanol). Nitrosation of **11** followed by reduction afforded 1-amino-2,5-diethyl-2,5-dimethylpyrrolidine **13**, (97%

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(12) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978.

(13) Murov, S. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973.

(14) We thank William Lambert and Professor Ahmed Zewail at Caltech for their generous assistance.

(15) Assuming $\epsilon = 10^{-2}$, $c = 1$ M, $l = 1$ c, $A = 0.01$ for an S_0–T_1 absorption.

(16) The ESR spectrum of a triplet 1,1-diazene would be expected to exhibit a line in the region of 5000–8000 G for a microwave frequency of 9.234 GHz.[17]

(17) Wasserman, E. *Prog. Phys. Org. Chem.* **1971**, *8*, 319.

(18) The diffusion-controlled rate constant in $CFCl_3$ at −78 is 9.3×10^9 L/(mol s).

(19) Renzepis, P. M. *Chem. Phys. Lett.* **1969**, 3717. For an $E_T = 39$ kcal, see: Kerkstroeter, W. G. *J. Amer. Chem. Soc.* **1975**, *97*, 4161.

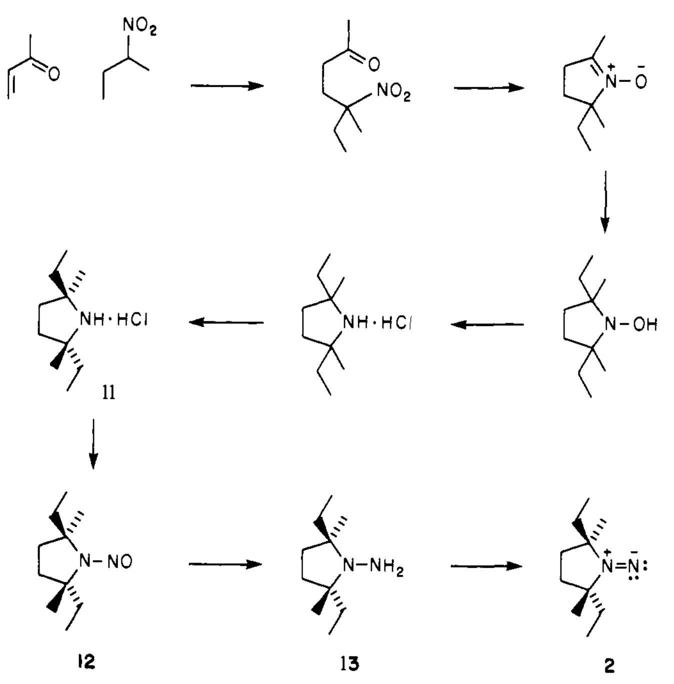
(20) Synthesized by the method of Greene: Greene, F. D.; Gilbert, K. E. *J. Org. Chem.* **1975**, 40, 1409.

(21) Porter, N. A. Ph.D. Thesis, Harvard University, Cambridge, MA, 1969.

(22) Bartlett, P. D.; Porter, N. A. *J. Am. Chem. Soc.* **1968**, *90*, 5317.

(23) For a discussion of spin correlation effects in 1,2-diazenes, see: Engel, P. S. *Chem. Rev.*, **1980**, *80*, 99.

(24) Kornblum, N.; Larson, H. O.; Blackwood, K. K.; Mooberry, O. D.; Oliveto, E. P.; Grahan, G. E. *J. Am. Chem. Soc.* **1956**, *78*, 1497.

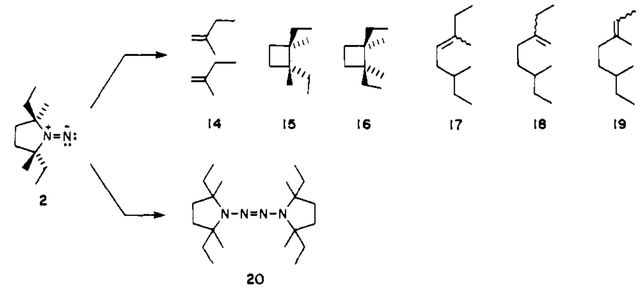


dl, 3% *meso*). The (+)-α-methoxy-α-trifluoromethylphenylacetate amide[25] of the unresolved *dl* hydrazine showed two peaks of near equal intensity separated by 0.12 ppm at −69.5 ppm (relative to $CFCl_3$) in the ^{19}F NMR and are assigned to the diasteromeric trifluoromethyl groups.

Addition of *tert*-butyl hypochlorite to a stirred solution of hydrazine **13** and triethylamine in anhydrous dimethyl ether at −78 °C affords, in addition to an insoluble white precipitate (Et_3NHCl), a red solution of 1,1-diazene **2** which is stable for days at −78 °C. Filtration at −78 °C followed by low-temperature chromatography (−85 °C) on basic alumina and concentration in $CFCl_3$ yields a solution of >98% 1,1-diazene **2**, <2% tetrazene, and small amounts of dimethyl ether. Low-temperature infrared (−78 °C) spectroscopy revealed an absorption at 1630 cm^{-1}, which disappeared on warming and is assigned to the N=N stretch.

The absorption and fluorescence spectra of **2** are shown in Figure 2. The absorption spectrum reveals a structured absorption with λ_{max} at 507 nm and a 0–0 band at 568 nm ($\epsilon = 20 \pm 2$, $CFCl_3$).[10] The vibrational spacing is 1270 cm^{-1}. The emission spectrum has a 0–0 band and λ_{max} at 620 nm ($CFCl_3$). The spacing between the peaks at 620 and 690 nm corresponds to the N=N stretch of S_0 consistent with the 1630-cm^{-1} stretch obtained from the infrared spectrum of **2**. The shapes of the absorption and emission spectra are different. The absorption and emission spectra of **2** are very similar to those of 1,1-diazene **1**. The fluorescence rate constant (k_F) for S_1 (n,π*), calculated from the integrated absorption spectrum, is 1×10^5 s^{-1}.[12] ϕ_F of 1,1-diazene **2** in MTHF is 9×10^{-3} at −196 °C, similar to the ϕ_F of 1,1-diazene **1**.

Thermal decomposition of a degassed chromatographed solution of **2** at 0 °C (0.1 M in $CFCl_3$) yields hydrocarbons **14–19** and tetrazene **20**. The ratio of cleavage/closure products is 0.8, not too different from that found in the thermal fragmentation of **1**. The retention of stereochemical integrity in the closure product is high (98%), analogous to the Bartlett–Porter 1,2-diazene result and consistent with behavior expected of a singlet 1,4-biradical with tertiary radical centers where $k_{(rotation)} << k_{(closure)}$.[26]



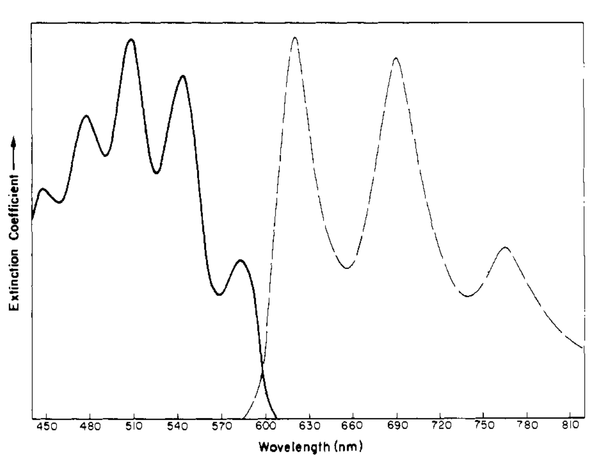


Figure 2. Absorption spectrum of **2** at −78 °C (—). Fluorescence spectrum of **2** at −196 °C (---).

Table II. Products from 1,1-Diazene 2

conditions	14	15	16	17-19	20
thermal, 0 °C	44	51	2	3	5
direct, −78 °C	47	45	2	5	399
sensitized, −78 °C	73	17	8	2	720

Direct and sensitized photolyses of 1,1-diazene **2** were carried out in the manner described for 1,1-diazene **1**, affording hydrocarbons **14–19** and tetrazene **20**. Product distributions from the thermolysis and direct and photosensitized photodecompositions are shown in Table II.

Analogous to the thermal reactions, direct irradiation of 1,1-diazene **2** affords substituted cyclobutanes with a high degree of retention of configuration and a butene/cyclobutane ratio of approximately 1.0. Triplet-sensitized photolysis results in loss of configuration in the cyclobutanes and a butene/cyclobutane ratio of 3. These results can be interpreted in terms of a mechanism similar to that proposed by Barlett and Porter[22] for the corresponding 1,2-diazene (see Scheme I).

In this scheme, the thermally generated singlet biradical behaves in a stereospecific manner and is characterized by $k_{(rotation)} << k_{(closure)}$. From the sensitized photodecomposition, the triplet biradical (conservation of spin) behaves in a much less stereospecific manner and is characterized by $k_{(isc)} \sim k_{(rotation)}$[27]. This rate determining triplet to singlet isc[28] allows some conformational equilibration to take place in the triplet 1,4-biradical and results in substantial loss of stereochemical integrity in the cyclobutane products as well as a higher cleavage/closure product ratio. Because direct irradiation of 1,1-diazene **2** affords closure products with high stereospecificity characteristic of singlet 1,4-biradical behavior, we conclude that the S_1 (n,π*) state of **2** (and by extension **1**) is characterized by $k_{isc} << k_{N_2}$.

An alternative mechanism for loss of stereochemical integrity in triplet photolysis is one bond cleavage from the T_1 (n,π*) state of 1,1-diazene **2** to yield a triplet diazenyl biradical. If rotation

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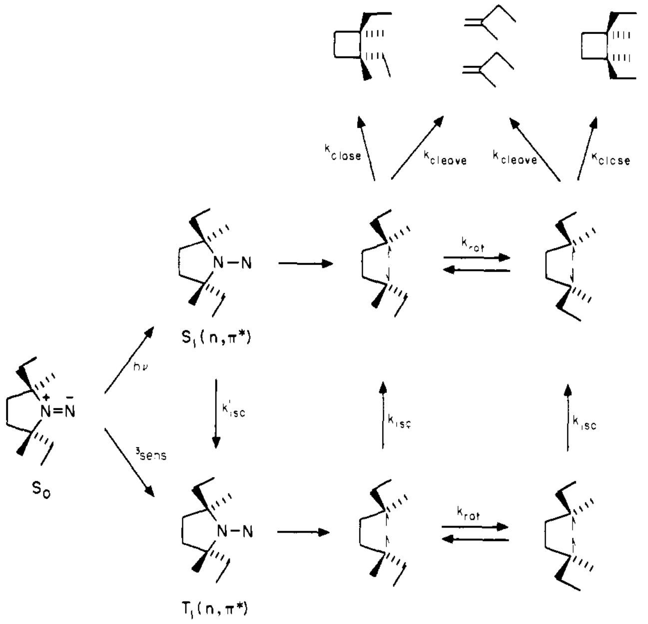
[25] Dale, A. D.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512.

[26] See: Dervan, P. B.; Uyehara, T.; Santilli, D. S. *J. Am. Chem. Soc.* **1979**, *101*, 2069 and references cited therein.

[27] It is curious that the ΔH_f of the thermal decomposition is above the calculated triplet state of the 1,1-diazene. Since thermolysis of the 1,1-diazene **2** affords high retention of configuration in the cyclobutane products consistent with a singlet 1,4-biradical, it is unlikely that the 1,1-diazene thermal decomposition proceeds via a triplet state.

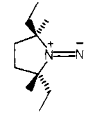
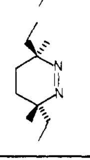
[28] Spin inversion is held to be rate determining in 1,4-biradicals from ketone photolysis. (a) Small, R. D., Jr.; Scaino, J. C. *J. Phys. Chem.* **1977**, *81*, 2126. (b) Closs, G. L. *Adv. Magn. Reson.* **1974**, *7*, 157. (c) Doubleday, C., Jr. *Chem. Phys. Lett.* **1981**, *77*, 131. (d) Scaiano, J. C. *Tetrahedron* **1982**, *38*, 819.

Scheme I. The Bartlett–Porter Mechanism Applied to 1,1-Diazene 2[a]



[a] For economy of space we have not drawn all possible conformational isomers about the 2–3 bond in the 1,4-biradical.

Table III. Stereochemistry of Cyclobutane Products from 1,1- and 1,2-Diazenes

diazene	decompn mode	temp, °C	retn of confign, %	ref
	thermal direct sensitized	0^a -78^a -78^a	98 96 68	*c* *c* *c*
	thermal direct sensitized	145^b 25^b 25^b	98 97 65	*d* *d* *d*

[a] $CFCl_3$. [b] Benzene. [c] This work. [d] Reference 22.

in the diazenyl biradical is competitive with cleavage of the C–N bond, one might expect some crossover in the stereochemistry of the cyclobutane products. This mechanism would place no constraints on k_{isc} for the substituted 1,4-biradical. There is good evidence for the existence of thermally generated 1-norbornyl- and phenyldiazenyl radicals.[29] In addition, recent results suggest that the T_1 (n,π^*) state of one acyclic 1,2-diazene decomposes via a diazenyl radical intermediate whereas the S_1 (n,π^*) state does not.[30,31] In both mechanisms, the stereospecificity in the cyclobutane products on direct irradiation may reflect simultaneous two-bond cleavage. However, a diazenyl intermediate from T_1 implicates different decomposition mechanisms rather than a spin correlation effect S_1 and T_1 on a common 1,4-biradical intermediate.

Table III shows a comparison of the results for the thermal and photochemical decomposition of 1,1-diazene **2** with the corresponding 1,2 isomer **10**.[22] Although the temperatures of photodecomposition differ by 100 °C, both diazenes show similar amounts of crossover in the cyclobutane photoproducts.

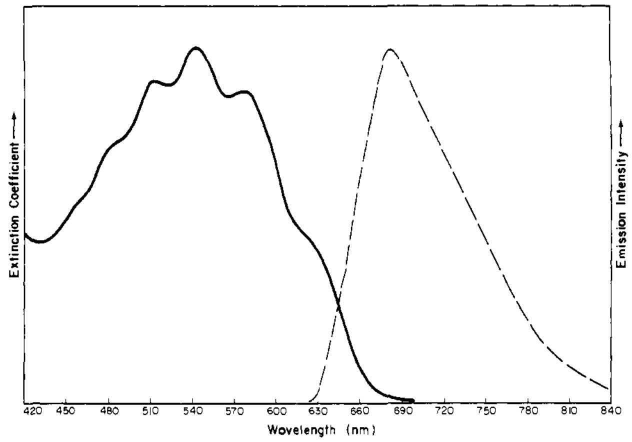


Figure 3. Absorption (—) and fluorescence (---) spectra of **3** in $CFCl_3$ at −78 and −196 °C, respectively.

One interpretation of this result is that the ratio k_{rot}/k_{isc} for the tertiary substituted 1,4-biradicals is relatively temperature insensitive. This would require that rotation at tertiary biradical centers and intersystem crossing have similar barrier heights and preexponential terms. This apparent barrier to intersystem crossing in the triplet 1,4-biradical may be evidence for a *conformational dependence on the biradical intersystem crossing rates*.

Assuming k_{isc} is also less than k_{N_2} for 1,1-diazene **1**, it is possible to define the deactivation pathways and rate constants for decomposition of S_1 of 1,1-diazene **1**: $k_{ic} = 1.5 \times 10^8$ s^{-1}; $k_{DIM} > 4 \times 10^7$ L mol^{-1} s^{-1}; $k_{N_2} > 3 \times 10^5$ s^{-1}; $k_F = 3 \times 10^5$ s^{-1}. The large internal conversion rate and slow intersystem crossing rate for **1** are consistent with the small S_0–S_1 gap and relatively large S_1–T_1 gap, respectively. A fluorescence rate constant of 3×10^5 s^{-1} is typical of n,π^* symmetry forbidden transitions. The k_{N_2} value of 3×10^5 s^{-1} at −78 °C can be extrapolated to 25 °C. Assuming an A factor of 10^{13} would require an E_a of 6.7 kcal/mol, affording $k_{N_2} = 1.2 \times 10^8$ s^{-1} (25 °C). For S_1, $k_{DIM} > 4 \times 10^7$ L mol^{-1} s^{-1} (−78 °C) is a minimum of 12 orders of magnitude faster than for S_0 dimerization, $k_{DIM} = 10^{-5}$ L mol^{-1} s^{-1}.

Finally, products consistent with Norrish type II chemistry of photoexcited **2** were not observed by VPC or low-temperature ^{1}H NMR. Neither direct nor sensitized photolysis of 1,1-diazene **1** in the presence of high concentration of hydrogen donors (e.g., 1,4-cyclohexadiene) yielded products resulting from hydrogen abstraction.[32] Triethylamine did not quench S_1 to T_1 of **1** or alter product ratios within experimental error. Direct and sensitized photolysis of **1** in the presence of *cis,trans*-hexadiene, *cis*-2-butene, and *cis*-1-ethoxy-1-butene did not afford aziridine adducts or isomerized butenes.

***N*-(2,2,6,6-Tetramethylpiperidyl)nitrene (3).** Addition of *tert*-butyl hypochlorite to a stirred solution of 1-amino-2,2,6,6-tetramethylpiperidine and triethylamine in anhydrous dimethyl ether at −78 °C affords, in addition to an insoluble white precipitate (Et_3NHCl), a purple solution of 1,1-diazene **3** (λ_{max} 543 nm (ϵ 18 ± 3, Et_2O) that is stable for −78 °C.[8] This solution is filtered at −78 °C, further purified by low-temperature chromatography (−85 °C) on basic alumina, and concentrated in $CFCl_3$. Low-temperature ^{1}H NMR spectroscopy (−60 °C, $CFCl_3$) reveals a solution of 70% 1,1-diazene **3**, 25% 1-amino-2,2,6,6-tetramethylpiperidine, and 5% tetrazene **25**. Solutions of 1,1-diazene **3** thus purified are stable at −78 °C in the absence of triethylamine. The absorption and fluorescence spectra of 1,1-diazene **3** in $CFCl_3$ are shown in Figure 3. The absorption spectrum has a λ_{max} at 543 nm and a 0–0 band at 620 nm.[10] The vibrational spacing is 1113 cm^{-1}.

The fluorescence spectrum, corrected for instrument response to 900 nm, has only a single maximum at 684 nm, which also

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[29] Parker, N. A.; Dubay, G. R.; Green, J. G. *J. Am. Chem. Soc.* **1978**, *100*, 920.

[30] Engel, P. S.; Bishop, D. J.; Page, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 7009.

[31] Both energy-localized (n,π^*) states and vibrationally excited ground states have been postulated in the photodecompositions of the isomeric 1,2-diazenes. See: Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.

[32] 1,1-Diazene **1** was found to be unstable in the presence of 1,3-propanethiol and tri-*n*-butyltin hydride.

Table IV. Hydrocarbon Products from 1,1-Diazene 3

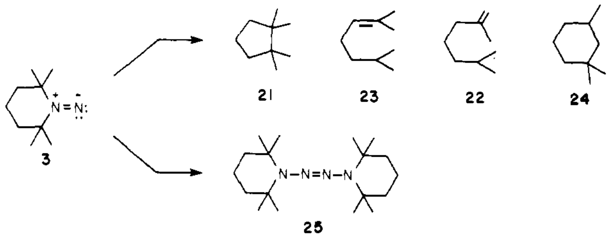
conditions[a]	21	22	23	24
thermal, 0 °C	24	10	61	5
thermal, −20 °C	24	7	65	4
direct, $h\nu$, −78 °C	29	3	68	0

[a] Et_2O.

corresponds to the 0–0 band. A second maximum would appear at 767 nm (γ[N=N] 1595 cm^{-1}) and should be readily discernible. The λ_{max} of the absorption and fluorescence spectra differ by 141 nm. On warming to 0 °C and subsequent recooling to −196 °C the fluorescence signal disappears. As was the case with diazenes **1** and **2**, the absorption and fluorescence spectra differ substantially in shape.

The fluorescence rate constant (k_F) for S_1 (n,π*) calculated from the integrated absorption spectrum is 9.9×10^4 s^{-1}. The fluorescence quantum yield ϕ_F at −196 °C in MTHF is 4×10^{-4}. The fluorescence lifetime τ_F at −196 °C was too short to be measured (<10^{-8} s), but from $\tau_F = \phi_F/k_F$, $\tau_F = 4 \times 10^{-9}$ s, an order of magnitude shorter than the lifetime for the five-membered ring 1,1-diazene **1**.

For photochemical studies, a degassed chromatographed solution of 1,1-diazene **3** (0.05 M in $CFCl_3$) was irradiated with visible light at −78 °C at >500 nm. After 12 h of irradiation at −78 °C the purple color had completely disappeared. Capillary VPC and ^{1}H NMR spectroscopy (−60 °C) revealed three hydrocarbon products, **21–23**, and tetrazene **25** in a ratio of 1:3



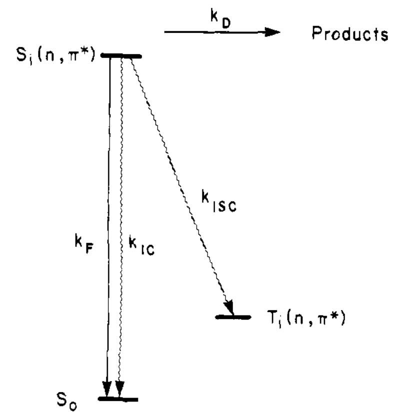
(Table IV). Triplet-sensitized photodecompositions could not be carried out due to overlap of the azulene sensitizer with 1,1-diazene **3** in the visible region.

The appearance of the same hydrocarbon products **21–23** in similar ratios from both the thermal and photochemical decomposition of 1,1-diazene **3** suggests a common intermediate. The fact that 1,1,3-trimethylcyclohexane is absent in the photolysis is significant. In our earlier studies on thermal decomposition of **3** we suggested that the appearance of 1,1,3-trimethylcyclohexane raised the issue of two possible competing decomposition pathways for the *thermal* fragmentation of **3**.[8d] The photolysis product ratios may reflect the behavior of the 1,5-biradical at −78 °C.

Summary

The recent syntheses and characterizations of persistent 1,1-diazenes have made possible a photochemical investigation of this reactive species. 1,1-Diazenes have a structured visible electronic absorption with 0–0 bands from 550 to 610 nm (ϵ = 15–20) fluoresce with ϕ_F of 10^{-4} to 10^{-2}. The fluorescence lifetimes of 1,1-diazenes **1** and **3** are $\tau_F = 2.3 \times 10^{-8}$ and 4×10^{-9} s (at −196 °C), respectively. The shapes of the absorption and fluorescence spectra of 1,1-diazene **1**, **2**, and **3** differ substantially. The λ_{max} of the absorption and emission spectra are displaced by 100 to 150 nm, revealing differences in the equilibrium S_1 and S_0 geometries. Direct and sensitized photodecompositions afford products from both unimolecular and bimolecular reactions. The unimolecular excited-state decompositions are consistent with extrusion of nitrogen to form the appropriate hydrocarbon biradical. Bimolecular tetrazene forming reactions, which probably result from the reaction of S_1 (and T_1) with S_0, proceed at a rate many orders of magnitude faster than dimerization of S_0. Five-membered cyclic 1,1-diazenes show a spin correlation effect on direct and sensitized irradiation, sugggesting $k_{isc} << k_{N_2}$ from S_1. The photochemical parameters for the persistent 1,1-diazenes studied are shown in Scheme II. Although T_1 has been shown to lie ≤31 kcal above S_0,[19] the precise S_0–T_1 gap remains unknown. The agreement of the results of the spin correlation study on *N*-(2,5-diethyl-2,5-dimethylpyrrolidyl)nitrene with those of the isomeric 1,2-diazene at different temperatures bears on a number of questions about the mechanism of diazene decompositions, the factors influencing S–T interconversion in biradicals, and the rates of these interconversions.

Scheme II[a]



[a] E (S_1) = 47–50 kcal (CH_2Cl_2); E (T_1) < 31 kcal; $k_F \sim 3 \times 10^5$ s^{-1}; $k_{IC} = 1.5 \times 10^8$ s^{-1} (−78 °C); $k_{N_2} > 3.4 \times 10^5$ s^{-1} (−78 °C); $k_{DIM} > 4.2 \times 10^7$ L mol^{-1} s^{-1} (−78 °C); $k_{isc} << k_{N_2}$; τ_F (1) = 2.3×10^{-8} s (−196 °C).

Table V

designation	description
Pennwalt 223	10 ft × $^1/_8$ in. stainless steel; 28% Pennwalt 223 on 80/100 Chrom R
Pennwalt 223	10 ft × $^1/_4$ in. glass, 28% Pennwalt 223 on 80/100 Chrom R
Carbowax 400	10 ft × $^1/_8$ in. stainless steel; 10% Carbowax 400 on 100/120 Chrom P A/W DMCS
ββ	20 ft × $^1/_8$ in. stainless steel; 10% β-oxydipropionitrile on 100/120 Chrom P A/W DMCS
ββ	10 ft × $^3/_8$ in. aluminum; 25% β-oxydipropionitrile on 50/80 Chrom P
SF-96	10 ft × $^3/_8$ in. aluminum; 25% SF-96 on 45/60 Chrom A
SF-96	10 ft × $^1/_8$ in. stainless steel; 10% SF-96 on SF-96 on 100/120 Chrom P A/W
SE-54	SE-54, capillary fused silica, 30 m × 0.25 mm
Carbowax 20M	Carbowax 20M, capillary fused silica, 15 m × 0.25 mm

Experimental Section

Melting points were determined using a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 257 infrared spectrophotometer. Proton nuclear magnetic resonance (NMR) spectra were obtained on a Varian EM-390, Jeol FX-90, or Brucker 500 spectrometer. Chemical shifts are reported as parts per million (ppm) downfield from tetramethylsilane in δ units and coupling constants are in hertz (Hz). Electronic spectra were obtained using a Cary 14 or Varian 219 spectrophotometer. Low-temperature IR and UV-vis cells have been previously described.[8] ESR spectra were recorded on a Varian Associates E-line spectrometer equipped with an Air Products and Chemicals Helitran LTD-3-110 liquid helium transfer apparatus with a 250-W mercury lamp. The emission spectra were taken with the assistance of members of Professor H. B. Gray's group at Caltech using a noncommercial spectrophotometer with a 250-W xenon source and Hamamatsu R-406 and R-955 PMTS. Fluorescence lifetimes were measured with the assistance of Professor A. Zewail's group at Caltech using a noncommercial apparatus consisting of a 1 nJ/pulse nitrogen pumped dye laser (0.3-cm^{-1} bandwidth, 10–15-ns pulse width) and IP28 PMT.

For analytical vapor phase chromatography (VPC) a Hewlett-Packard 5700A gas chromatograph equipped with a flame ionization detector and nitrogen carrier gas was used. The 0.125-in. packed stainless steel columns used in this instrument are listed in Table V. Quantitative VPC analysis was accomplished by using Hewlett-Packard 3370A electronic digital integrator. A Hewlett-Packard 5800 capillary gas chromatograph equipped with flame ionization detector and Hewlett-Packard 5880 series electronic integrator was also used; hydrogen/helium was used as carrier gas. The 0.25-mm packed fused silica columns used are listed in Table V. For preparative VPC, a Varian 920 instrument equipped with a thermal conductivity detector and helium carrier gas was used. The 0.375-in. packed aluminum columns used are listed in Table V. Detector response for hydrocarbons are assumed to be 1.0 relative to *n*-octane. Quantitative analyses of all other compounds was corrected for detector response.

Dibutyl ether and 2-propanol were distilled from sodium. Ethyl ether and 2-methyltetrahydrofuran were distilled from sodium benzophenone ketyl. Triethylamine was distilled from barium oxide. Chloroform and fluorotrichloromethane were passed through a short column of basic alumina. Deuteriochloroform used for obtaining 1,1-diazene NMR spectra was passed through a short column of basic alumina. Propane and dimethyl ether used in low-temperature chromatography were dried over 4A molecular sieves. *tert*-Butyl hypochlorite was washed with 10% sodium carbonate, water, dried ($CaCl_2$), and distilled under nitrogen. 1-Amino-2,2,6,6-tetramethylpiperidine, 1-amino-2,5-diethyl-2,5-dimethylpyrrolidine, and 1-amino-2,2,5,5-tetramethylpyrrolidine were always purified by preparative VPC (Pennwalt 223) prior to use.

Combustion analyses were performed at Galbraith Laboratories, Knoxville, TN. Unless otherwise indicated, reactions were carried out under a positive pressure of nitrogen. Procedures for obtaining low-temperature IR, UV–vis, and NMR spectra of 1,1-diazenes have been described elsewhere.

5-Ethyl-5-nitrohexan-2-one. To a refluxing solution of 180 g (1.75 mol) of 2-nitrobutane and 13 mL Triton B in 250 mL of ether was added 123 g (1.75 mol) of methyl vinyl ketone over a 3-h period. The mixture was stirred at reflux for an additional 15 h, cooled, and acidified with a 10% HCl solution. The ethereal layer was separated, washed twice with water, washed with saturated sodium chloride solution, and dried (Na_2SO_4). The ethereal extracts were concentrated and distilled, giving 280 g (95%) of a pale yellow oil, 5-ethyl-5-nitrohexan-2-one: bp 111–113 °C (2.5 torr); IR (CCl_4) 2985, 1725, 1536, 1460, 1390, 1355 cm^{-1}; NMR ($CDCl_3$) δ 2.6–2.1 (m, 4 H), 2.1–1.7 (m, 2 H), 2.1 (s, 3 H), 1.5 (s, 3 H), 0.85 (t, 3 H). Anal. Calcd for $C_8H_{15}NO_3$: C, 55.47; H, 8.74; N, 8.08. Found: C, 55.55; H, 8.65; N, 8.04.

2,5-Dimethyl-2-ethyl-Δ^5-pyrroline Oxide. 5-Ethyl-5-nitrohexan-2-one (200 g, 1.16 mol) and ammonium chloride (77 g, 1.45 mol) in 2 L of water were heated to 65 °C with mechanical stirring. Zinc dust (117 g, 2.7 mol) was added in portions over 30 min, with the temperature of the reaction mixture being maintained at 65–70 °C. The mixture was stirred 2 additional h at 65 °C, cooled, and filtered. The aqueous filtrate was acidified with dilute HCl, concentrated to 500 mL, made basic with sodium hydroxide, and extracted (8 × 100 mL) with methylene chloride. The methylene chloride extracts were combined, dried (Na_2SO_4), and concentrated. The resulting oil was distilled, giving 114 g (71%) of a pale yellow oil, 2,5-dimethyl-2-ethyl-Δ^1-pyrroline oxide: bp 77–78 °C (0.25 torr); IR (CCl_4) 3440, 2980, 1603, 1460, 1395, 1370 cm^{-1}; NMR ($CDCl_3$) δ 2.5 (t, 2 H), 2.0 (s, 3 H), 2.1–1.5 (m, 4 H), 1.4 (s, 3 H), 0.85 ppm (t, 3 H). Anal. Calcd for $C_8H_{15}NO$: C, 67.96; H, 10.72; N, 9.92. Found: C, 67.90; H, 10.59; N, 9.94.

1-Hydroxy-2,5-diethyl-2,5-dimethylpyrrolidine. To a Grignard reagent prepared in the usual way from 120 g (1.1 mol) of ethyl bromide and 27 g (1.1 mol) of magnesium turnings in 500 mL ether was added, with mechanical stirring, a solution of 100 g (0.71 mol) of 2,5-dimethyl-2-ethyl-Δ^1-pyrroline oxide in 400 mL of ether at such a rate that the mixture refluxed gently. After addition was complete, the mixture was refluxed for 24 h and cooled to 0 °C, and a solution of 145 g of ammonium chloride in 600 mL of water was added slowly. After stirring for an additional 30 min, the ether layer was separated and the aqueous layer extracted (5 × 200 mL) with ether. The combined ethereal extracts were dried (Na_2SO_4), concentrated, and distilled, affording 50 g (52%) of a colorless oil, 1-hydroxy-2,5-diethyl-2,5-dimethylpyrrolidine: bp 83–85 °C (1.2 torr); IR (film) 3500, 2980, 1465, 1380, 1370 cm^{-1}; NMR ($CDCl_3$) δ 6.9 (s, 1 H), 1.8–1.2 (m, 8 H), 1.1 (s, 6 H), 0.85 ppm (t, 6 H). Anal. Calcd for $C_{10}H_{21}NO$: C, 70.10; H, 12.38; N, 8.17. Found: C, 70.04; H, 12.09; N, 8.16.

2,5-Diethyl-2,5-dimethylpyrrolidine Hydrochloride (11). A mixture of 25 g (0.18 mol) of 1-hydroxy-2,5-diethyl-2,5-dimethylpyrrolidine and 2 g of Raney nickel in 200 mL of methanol was hydrogenated on a Parr rocker at 26 °C and 50 psi H_2. The filtered reaction mixture was acidified with ethereal hydrogen chloride and the solvent removed to give 30 g of a brownish white crystalline precipitate. Recrystallization from 2-propanol/ether yielded 28 g (95%) of 2,5-diethyl-2,5-dimethylpyrrolidine hydrochloride (**11**): mp 200–205 °C; IR (CCl_4) 2930, 2710, 1460, 1390 cm^{-1}; NMR ($CDCl_3$) δ 9.3 (s, 1 H), 2.2–1.8 (m, 8 H), 1.6 (s, 6 H), 1.05 ppm (t, 6 H). The amine hydrochloride **11** was converted to 2,5-diethyl-2,5-dimethylpyrrolidine by dissolving in a 25% aqueous sodium hydroxide solution, extracting the resulting oil with ether, drying the ethereal extracts, and concentrating. Further purification by preparative VPC (Pennwalt, 180 °C) afforded 2,5-diethyl-2,5-dimethylpyrrolidine (>99%): IR (film) 3350, 2915, 1460, 1378, 1370 cm^{-1}; NMR ($CDCl_3$) δ 1.7–1.2 (m, 8 H), 1.0 (s, 6 H), 0.8 ppm (t, 6 H). Anal. Calcd for $C_{10}H_{21}N$: C, 77.34; H, 13.63; N, 9.02. Found: C, 77.60; H, 13.58; N, 8.99.

1-Nitroso-2,5-diethyl-2,5-dimethylpyrrolidine (12). To a stirred solution of 8 g (0.044 mol) of 2,5-diethyl-2,5-dimethylpyrrolidine hydrochloride in 100 mL of water at 85 °C was slowly added a solution of 15.6 g (0.23 mol) of sodium nitrite in 50 mL of water. The reaction temperature was maintained at 85 °C for 48 h, during which time a yellow oil formed. The reaction mixture was cooled, 30 mL of ether was added, and the layers were separated. The aqueous layer was extracted twice with ether. The combined ethereal extracts were washed with 10% HCl solution and saturated sodium chloride solution. The ethereal extracts were dried (Na_2SO_4) and concentrated, affording 7.0 g (92%) of a yellow oil, 1-nitroso-2,5-diethyl-2,5-dimethylpyrrolidine (**12**). This was further purified by VPC (Pennwalt, 220 °C): IR (CCl_4) 2930, 1470, 1380, 1370 cm^{-1}; NMR ($CDCl_3$) δ 2.1–1.5 (m, 8 H), 1.45 (s, 3 H), 1.35 (s, 3 H), 0.85 (t, 3 H), 0.75 (t, 3 H). Anal. Calcd for $C_{10}H_{20}N_2O$: C, 65.17; H, 10.94; N, 15.20. Found: C, 65.03; H, 10.91; N, 15.34.

1-Amino-2,5-diethyl-2,5-dimethylpyrrolidine (13). A slurry of 2.2 g (0.05 mol) of lithium aluminum hydride in 70 mL of 6:1 *n*-butyl ether/diethyl ether was heated under N_2 with distillation of solvent until the internal temperature reached 105 °C. A solution of 5 g (0.027 mol) of 1-nitroso-2,5-diethyl-2,5-dimethylpyrrolidine in 20 mL of *n*-butyl ether was then cautiously added over 1 h; the temperature was not allowed to rise above 110 °C. The temperature was maintained at 95 °C for an additional 4 h, and the reaction mixture was cooled to 0 °C and hydrolyzed by careful addition of a large excess of water. The layers were separated and the aqueous layer was extracted twice with ether. The combined organic extracts were extracted three times with 10% HCl solution. The combined acid extracts were made strongly basic with 20% sodium hydroxide solution and were extracted three times with ether. The ethereal extracts were combined and washed with saturated sodium chloride solution. The ethereal extracts were dried (Na_2SO_4) and concentrated, affording a colorless oil. This oil was further purified by distillation under reduced pressure at 25 °C, followed by preparative VPC (Pennwalt, 180 °C), affording 3 g (45%) of 1-amino-2,5-diethyl-2,5-dimethylpyrrolidine (**13**): IR (CCl_4) 3350, 3230, 2970, 1460, 1380, 1365 cm^{-1}; NMR ($CDCl_3$) δ 2.65 (s, 2 H), 1.70–1.20 (m, 8 H), 1.0 (s, 6 H), 0.85 (t, 6 H). This hydrazine **13** is air sensitive. Benzamide: Anal. Calcd for $C_{17}H_{26}N_2O$: C, 74.41; H, 9.55; N, 10.20. Found: C, 74.67; H, 9.32; N, 9.96.

1,1′-Azo-2,5-diethyl-2,5-dimethylpyrrolidine (20). 1-Amino-2,5-diethyl-2,5-dimethylpyrrolidine (**13**) (250 mg, 0.74 mmol) was stirred under an oxygen atmosphere for 24 h. The resulting colorless oil was warmed at 40 °C (0.05 torr) for 24 h to yield 42 mg (17%) of a white crystalline solid, **20**: mp 47–49 °C; IR (film) 2960, 1465, 1378, 1367 cm^{-1}; NMR ($CDCl_3$) 1.9–1.25 (m, 8 H), 1.15 (s, 6 H), 0.75 (t, 6 H), UV (2,2,5-trimethylpentane) 303 (ϵ 9780), 254 nm (ϵ 2130). Anal. Calcd for $C_{20}H_{40}N_4$: C, 71.35; H, 12.0; N, 16.64. Found: C, 71.39; H, 11.86; N, 16.65.

***dl*-1-Amino-2,5-diethyl-2,5-dimethylpyrrolidine (13).** The crude amine hydrochloride **11** was recrystallized from 2-propanol (–20 °C) to separate the meso and *dl* isomers. In a typical experiment 70 g of the amine hydrochloride was dissolved in 400 mL of 2-propanol. Approximately 35 g of *dl*-enriched amine hydrochloride crystallized out after 12 h at –20 °C. Recrystallization was repeated eight times until the *dl* isomer was obtained in 97% isomeric purity (the *dl* and meso isomers are distinguishable by 500-MHz ^1H NMR). The *dl*-2,5-diethyl-2,5-dimethylpyrrolidine hydrochloride was converted to *dl*-amino-2,5-diethyl-2,5-dimethylpyrrolidine by the methods described above. Capillary VPC (Carbowax 20M, 60 °C) indicated the hydrazine **13** was 97% *dl*, 3% meso.

Resolution of *dl*-2,5-Diethyl-2,5-dimethylpyrrolidine. The *dl* amine hydrochloride **11** was converted to the amine by methods described above and purified by preparative VPC (Pennwalt, 160 °C). Addition of 1 g of pure amine to a refluxing solution of 1.1 g of *d*-tartaric acid, 7.3 mmol, in 15 mL of 2-propanol gave on prolonged cooling 1 g of white precipitate. A second recrystallization yielded approximately 0.5 g of crystals. These crystals were dissolved in 10 mL of 20% aqueous potassium hydroxide and extracted with three 10-mL portions of ether. The ether solution was then dried (Na_2SO_4) and concentrated. The amine was collected by VPC (Pennwalt, 160 °C). A methanolic solution of the amine hydrochloride was obtained by titrating the amine with hydrogen chloride. The amine hydrochloride had the following rotations: $[\alpha]^{20}$

4.80°, $[\alpha]^{20}$ 0.78° (*c* 0.39, methanol). The assignment of the *dl* isomer was confirmed by reaction of racemic *dl*-1-amino-2,5-diethyl-2,5-dimethylpyrrolidine with (+)-α-methoxy-α-trifluorophenylacetyl chloride by the method of Dale and Mosher.[25] ^{19}F NMR revealed two singlets separated by 0.12 ppm centered at −69.5 ppm (relative to $CFCl_3$) corresponding to the diastereomeric trifluoromethyl groups.

General Procedure for Generation and Purification of 1,1-Diazenes. All apparatus must be base-washed and thoroughly dried. Into an argon-purged 25-mL flask was placed 1.75 mmol of the appropriate 1,1-dialkylhydrazine. The flask was cooled to −78 °C, and 12–15 mL of dry methyl ether was added followed by 1.25 mmol of triethylamine. With rapid stirring 1.6 mmol of *tert*-butyl hypochlorite was added dropwise over 15 min. Color appeared almost immediately and was fully developed within 10 min. The reaction mixture was stirred 1 h at −78 °C and then transferred via 18-gauge Teflon tubing to an argon-purged jacketed filter funnel precooled to −78 °C. The mixture was filtered under vacuum into a 25-mL three-neck flask precooled to −78 °C and equipped with serum cap and gas inlet tube. The solution was then concentrated to 2–3 mL for chromatography.

Deactivated basic alumina was prepared by washing 150 g of Woelm Activity I neutral alumina three times with 150 mL of 20% sodium hydroxide solution and decanting. After being washed three times with 150 mL of distilled water, the alumina was washed three times with methanol and dried 12 h at 350 °C.

A jacketed low-temperature chromatography column was equipped with a 200-mL three-neck round-bottom flask (with serum cap, gas inlet and 3–5 g of potassium carbonate). The column was charged with 30 g of deactivated basic alumina and capped. After the column was purged with argon, the jacket was filled with acetone and cooled to −88 °C by addition of liquid nitrogen with stirring. The column was wetted and rinsed through with 40 mL of dry propane (cooled to −78 °C), added by means of a double-ended needle. The concentrated 1,1-diazene solution was carefully placed on the column via a double-ended needle and allowed to percolate onto the adsorbent. Elution was begun with 2:3 dimethyl ether/propane using a positive pressure of argon at the column head to maintain a drip rate of 1–2 drops/s. When the colored band reached the bottom of the column, elution was halted by releasing the argon pressure. The collection flask was opened to a positive argon pressure and the forerun withdrawn via a double-ended needle into an evacuated flask cooled to −78 °C. Elution was resumed until two-thirds of the colored band had been collected. This colored solution was drawn off into a precooled (−78 °C), argon-purged 100-mL round-bottom flask equipped with serum cap argon/vacuum inlet, 3–5 mL of solvent, and 3–5 g of potassium carbonate. The propane/methyl ether was then removed under reduced pressure and argon admitted to the flask, leaving a concentrated diazene solution. This procedure afforded 1,1-diazenes **1** and **2** with ≤2% tetrazene and small amounts of dimethyl ether. 1,1-Diazene **3** contained 20–40% 1-amino-2,2,6,6-tetramethylpiperidine, 5–10% tetrazene, and small amounts of dimethyl ether. Not all chromatographies gave consistent results, therefore aliquots of all samples were checked by low-temperature ^{1}H NMR (−60 °C) prior to use.

Emission Spectroscopy and Determination of Photochemical Parameters. Approximately 1.5 mmol of the appropriate hydrazine was oxidized, filtered, chromatographed, and concentrated to 5–10 mL of solvent. Dry argon was admitted to the flask and 0.3 mL of the 1,1-diazene solution transferred via 18-gauge Teflon tubing into argon purged 5 mm NMR tubes precooled to 78 °C. For emission spectroscopy, the sample tubes were then placed in a jacketed liquid nitrogen dewar at −196 °C and the spectra were recorded with a noncommercial spectrophotometer in Professor H. B. Gray's group at Caltech. Excitation wavelength was 520 nm, using a 250-W xenon source and Hamamatsu R406 PMT. Response factors for the R406 PMT are 0.775 (500 nm), 0.835 (550 nm), 0.82 (600 nm), 0.785 (650 nm), 0.76 (700 nm), 0.58 (750 nm), 0.440 (800 nm), 0.325 (860 nm), and 0.235 (900 nm). No emission (phosphorescence) was present other than fluorescence from 500 to 1100 nm (R406). Saturated azulene and benzophenone solutions of **1** at −78 °C were prepared by transferring **1** into NMR tubes containing an excess of sensitizer. Emission spectroscopy of these solutions at −196 °C again revealed no emission signals from 600 to 1100 nm (R406) other than fluorescence. Samples for quantum yield determinations were prepared by dilution of a degassed chromatographed solution of 1,1-diazene ($CFCl_3$) 1/10 in the appropriate degassed solvent (argon purged). Concentrations were determined by measuring the absorbance of 4-mL aliquots of 1,1-diazene solutions. Fluorescence quantum yields in 2-methyltetrahydrofuran were determined at −196 °C by comparing the corrected integrated emission band of the 1,1-diazene with that of rubrene (ϕ_f = 1),[13] using an excitation wavelength of 480 nm. All other ϕ_f were determined relative to **1** in 2-methyltetrahydrofuran. Lifetimes of similarly prepared 1,1-diazene solutions were measured by the single photon counting technique with a noncommercial instrument made available by Professor A. Zewail's group at Caltech.[14]

Samples for ESR experiments were prepared as described above with both 2-methyltetrahydrofuran and cyclohexane as solvents. Solutions of 1,1-diazene and 1,1-diazene saturated with either azulene of benzophenone were irradiated at 10 and 88 K with a 250-W mercury xenon lamp filtered through water and Pyrex. The only feature in the spectrum is a strong doublet absorption at 3300 G which increases with time, presumably due to tetrazene decomposition. Solutions of tetrazene under the same conditions yield the same result.

Samples for determination of ϕ_{N_2} were prepared as described above and introduced into the precooled (−78 °C) low-temperature UV–vis cell. The absorbance spectrum was then recorded. The cell was then irradiated with a 1000-W xenon lamp; water, Pyrex, and Corning filters CS3-70 and CS4-96 were used. Transmitted light and incident light were measured by use of a Scientech laser power meter (Model 360001). Initial concentrations of 1,1-diazene were 0.05–0.1 M and photolyses were carried out to 5% conversion as determined by absorbance spectra. ϕ_D for 2,3-diazabicyclo[2.2.1]hept-2-ene was found to be 0.9, which is close to the literature value of 1.0.[33]

Products from the Thermal and Photochemical Decompositions of 1,1-Diazenes 1, 2, and 3. The identification and analysis of the hydrocarbon and tetrazene products from 1,1-diazenes **1** and **3** have been described earlier. Seven products were found when **2** (65% *dl*, 35% meso) was decomposed thermally or photochemically in $CFCl_3$. Analytical 0.125-in. VPC (Carbowax 400, 80 °C) revealed 2-methyl-1-butene (**14**), 1,2-diethyl-1,2-dimethylcyclobutanes (**15** and **16**) (inseparable), and octenes **17**–**19**. 2-Methyl-1-butene (**14**) was identified by co-injection of an authentic sample (Matheson). Preparative VPC (ββ, 30 °C) afforded a sample of **14** whose NMR was identical to that of authentic 2-methyl-1-butene (Matheson): ($CDCl_3$) δ 4.7 (s, 2 H), 2.0 (m, 2 H) 1.7 (s, 3 H), 1.05 (t, 3 H). *cis*- and *trans*-1,2-diethyl-1,2-dimethylcyclobutanes (**16** and **15**) eluted as one peak on a 0.125-in. Carbowax 400 column (80 °C). The retention time was identical with that of an authentic sample of *trans*-1,2-diethyl-1,2-dimethylcyclobutane (**15**). Preparative VPC (SF-96, 80 °C) revealed the presence of both cis and trans isomers by comparison of NMR to literature values: (CCl_4) δ 1.7 −1.2 (m) 1.02 (s, trans), 0.98 (s, cis), 0.75 (t). The mass spectrum reveals a parent peak at 140.15 with a base peak, *m/e* 70. The cis and trans cyclobutanes could be separated on a 30-m SE-54 fused silica capillary VPC column (35 °C). Assignment of stereochemistry was made by co-injection of authentic *trans*-1,2-diethyl-1,2-dimethylcyclobutane **15**. *cis*- and *trans*-3,6-dimethyl-3-octene (**17**) and 2-ethyl-5-methyl-1-heptene (**18**) eluted together on a 0.125-in. Carbowax 20M column (80 °C). Preparative VPC (Carbowax 20M, 100 °C) revealed the presence of **17** and **18**, which were identified by comparison of the NMR spectra with those of authentic samples.[34,35] 3,6-Dimethyl-2-octene (**19**) was separable from **17** and **18** and was identified by comparison of the NMR spectrum with that of authentic **19**. The alkenes could not be further separated by capillary VPC on either 30 m SE-54 or 50 m Carbowax. Co-injection techniques on 30 m SE-54 verified the assignments of these alkenes. **17**–**19** eluted as one peak on SF-96 (100 °C), affording a sample whose elemental agreed with the formula $C_{10}H_{20}$. Anal. Calcd for $C_{10}H_{20}$: C, 85.60; H, 14.39. Found: C, 85.67; H, 14.21. Hydrogenation of this mixture in a manner similar to that described for *trans*-1,2-divinyl-1,2-dimethylcyclobutane yielded one alkane (SF-96, 120 °C): NMR ($CDCl_2$), δ 1.5–1.0 (m, 10 H), 0.85 (m, 12 H). Tetrazene was identified by ^{1}H NMR.

***trans*-1,2-Diethyl-1,2-dimethylcyclobutane.** *trans*-1,2-Dimethyl-1,2-divinylcyclobutane was synthesized by the method of Hammond, Liu, and Turro.[36] The cyclobutane was separated from a mixture of hydrocarbons by distillation through a Teflon spinning band column, yielding 1 g (99% pure) of *trans*-1,2-dimethyl-1,2-divinylcyclobutane: NMR ($CDCl_3$) δ 6.0–4.7 (m, 6 H), 2.2–1.3 (m, 4 H), 1.1 (s, 6 H). This cyclobutane (1 g) in 60 mL of glacial acetic acid in the presence of 0.1 g of platinum oxide was hydrogenated at 25 °C at atmospheric pressure. The solution was diluted with water and extracted with pentane. The combined pentane extracts were washed with water, dried (Na_2SO_4), and concentrated. The resulting oil was purified by VPC (SF-96, 120 °C), yielding 0.8 g (80%) of *trans*-1,2-diethyl-1,2-dimethylcyclobutane (**15**), which was

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(33) Steel, C. *J. Phys. Chem.* **1963**, *67*, 1779.

(34) 3,6-Dimethyl-3-octene **17** and 3,6-dimethyl-2-octene **19** (with <5% **18**) were synthesized independently via conversion of 3-methyl-1-pentanol to 1-bromo-3-methylpentane followed by a Grignard with 2-butanone and subsequent dehydration. VPC (Carbowax 20M, 100 °C) was used to separate **17** (<5% **18**) and **19**.

(35) 2-Ethyl-5-methyl-1-heptene (**18**) was synthesized independently via a 1,4 addition of 2-butylmagnesium bromide to ethyl vinyl ketone (in the presence of cuprous chloride) followed by a Wittig reaction with triphenylphosphine methylene. **18** was purified by VPC (Carbowax 20M, 100 °C).

(36) Hammond, G. S.; Liu, W.; Turro, N. J. *J. Org. Chem.* **1963**, *28*, 3297.

shown by proton NMR and IR to be identical with *trans*-1,2-diethyl-1,2-dimethylcyclobutane reported by Barlett and Porter.[22] IR (film) 2990, 1460, 1365 cm^{-1}; NMR (CCl_4) δ 1.7–1.2 (m, 8 H), 1.02 (s, 6 H), 0.9–0.6 (t, 6 H).

Photodecomposition of 1, 2, and 3. Degassed chromatographed solution of **1**, **2**, and **3** were sealed in base-washed, argon-purged, precooled (−78 °C) 5-mm NMR tubes. Sensitizers were added to the tubes before addition of 1,1-diazene. In all photochemical decompositions two identical samples were prepared; one was photolyzed at −78 °C and the other remained in the dark at −78 °C. ^1H NMR spectra (−60 °C) were taken before and after photolysis to ensure that all decomposition of diazene arose from photolysis. In addition, the 1,1-diazenes were shown to be stable to partial photodecomposition. Photolyses were carried out at −78 °C (hexane, dry ice) in an evacuated quartz dewar. For direct photolyses of 1,1-diazene **1** and **2** a water filter, Pyrex filter, and two Corning glass filters, CS-370 and CS-496, were used (466–610 nm). For sensitized photolyses of **1** and **2**, a water filter, Pyrex filter, and Corning glass filter CS2-59 (>608 nm) were used. For direct studies on 1,1-diazene **3** Corning filter CS-251 was used. For sensitized photolysis, **1** and **2** were irradiated in the absence of azulene at >608 nm and shown to be photostable. All solution were photolyzed with a 1000-W argon arc lamp until the diazene had completely decomposed. Tetrazene/hydrocarbon ratios were determined by ^1H NMR (−60 °C). Hydrocarbon ratios were determined by a combination of 0.125-in. analytical VPC and capillary VPC. Solutions of 1,2-diazene **9** in $CFCl_3$ were degassed by three freeze–pump–thaw cycles in 5-mm NMR tubes and sealed. Photolyses were done at −78 °C (hexane/dry ice) in an evacuated quartz dewar using a water filter, Pyrex filter, and WF-335 Schott filter (>330 nm). Photolyses were halted at approximately 50% completion and analyzed in a manner identical with that of **1**. Triplet-sensitized photolyses were done in an identical manner with 0.05 M thioxanthone as a sensitizer.

Registry No. 1, 73331-62-1; *dl*-**2**, 83350-57-6; **3**, 66337-86-8; *dl*-**11**, 83350-62-3; *meso*-**11**, 83350-67-8; *dl*-**12**, 83350-64-5; *meso*-**13**, 83350-58-7; *dl*-**13**, 83350-66-7; (+)-**13**·HCl, 83350-70-3; (+)-**13**, 83350-68-9; (+)-**13**·(*d*)-tartrate, 83350-69-0; **20**, 83350-65-6; *dl*-ethyl-5-nitrohexan-2-one, 83350-59-8; 2-nitrobutane, 600-24-8; methyl vinyl ketone, 78-94-4; *dl*-2,5-dimethyl-2-ethyl-Δ^5-pyrroline oxide, 83350-60-1; ethyl bromide, 74-96-4; *dl*-1-hydroxy-2,5-diethyl-2,5-dimethylpyrrolidine, 83350-61-2; *dl*-2,5-diethyl-2,5-dimethylpyrrolidine, 83350-63-4; azulene, 275-51-4; thiaxanthene, 492-22-8; 3,4,5,6-tetrahydro-3,3,6,6-tetramethylpyridazine, 19403-24-8.

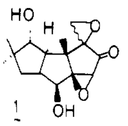
Palladium-Mediated Cycloaddition Approach to Cyclopentanoid Natural Products. (±)-Albene

Barry M. Trost* and Patrice Renaut

Contribution from the McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received March 24, 1982*

Abstract: A five-step synthesis of (±)-albene from 2,3-dicarbomethoxynorbornene utilizes the palladium-catalyzed cycloaddition of 2-((trimethylsilyl)methyl)-3-acetoxy-1-propene as the key reaction. Deoxygenation to the hydrocarbon takes advantage of the treatment of phosphoramidates with lithium. This procedure nicely resolves the problems of conversion of a ketone to an olefin and a neopentyl ester to a methyl group, which permits both types of modifications in a single stroke.

Polycondensed cyclopentanoid natural products represent an increasingly important class. In the tricycles, several different ring fusions occur among the sesquiterpenes as represented by **1**–**4**.[1–6] Outside of the hirsutanes as illustrated by coriolin **1**, none of these carbon skeletons were known among natural products prior to 1972.[7] The growing recognition of their importance mandates the development of efficient synthetic strategies. A cycloaddition approach to these as well as other cyclopentanoid



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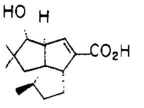

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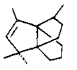

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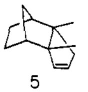

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